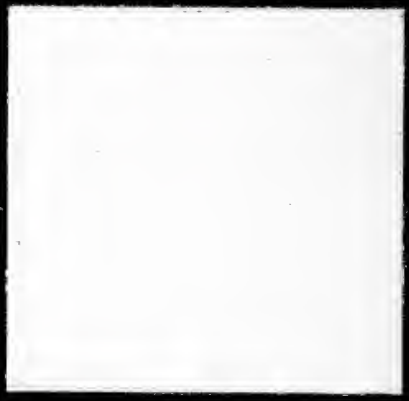

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METAL-COLOURING AND BRONZING

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METAL-COLOURING AND BRONZING

BY

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PREFACE

The attention of the author was directed to the subject of Bronzing some years back, and more particularly about eighteen months ago, by the apparent absence of any reliable information on the subject in this country. It is a subject in which those engaged in metal trades, especially in Birmingham, should be deeply interested, as that city was formerly considered to be one of the chief centres for the production of beautiful colours on metal work. A member of the Birmingham Technical School Committee, Mr. W. J. Davis, suggested to me that we should endeavour to improve the ordinary methods of working by establishing a class for the cultivation of this special branch of industry, and for studying in a systematic manner the principles on which the actions are based, so as to attempt to bring back the almost lost art to its former home, and, if possible, to greatly expand it in beauty and usefulness.

The present work is a record of the investigations carried out by means of many hundreds of experiments in every way that seemed likely to yield reliable information. The first thing was to find out, by inquiries in different

directions, and by reference to works which were likely to contain any information on the subject, what others had done, and how much of their work was published. A great number of recipes were thus collected, many of them bearing the stamp of age by the quaintness of the wording and the old-fashioned way in which different chemical bodies were named. Some were in quite a modern garb, as though they had been recently discovered, but in many cases their effectiveness was doubtful.

The experiments have been carried on almost uninterruptedly for eighteen months by the author and his colleague, Mr. T. J. Baker, who has conducted the greater part of the experiments with the assistance of Mr. A. Hiorns, jun.

Our aim has been to take nothing for granted, but to test every method in various ways by direct trials, and to faithfully record such results as were likely to be useful to our students and to any others who desire the information.

It is possible that, in cases where we have failed to obtain a good effect from a given solution, the fault may have been in the manipulation rather than in the reagent, and as this work is intended to stimulate further inquiry, as well as to give the results of our experience to the public generally, some other workers may succeed where we have failed, and this is the reason for recording some methods, recommended by others, but which proved to be useless under the conditions in which our experiments were performed.

In several instances we have found a certain solution barren of good results when first tried, but after perhaps several months of additional experience the secret of success has been discovered, and an apparently worthless

method found to be a very useful one. Sometimes it was the right temperature, or the proper strength of the solution that was needed, but more often the non-success has resulted from an excess of acid or alkali, as the preponderance of one or other of these chemical conditions may altogether alter the result. In some cases it is essential that the bronzing solution shall be perfectly neutral in character, as the deposit is dissolved if any acid or alkali is present in excess.

The term *Bronzing*, as now understood, may be applied to the formation of any kind of colour on metals for artistic effects, but as the word seems hardly applicable to those cases where one metal is deposited upon another by electrical or other means—as, for example, the deposition of copper or brass upon iron or zinc—the term *Metal-colouring* has been adopted as embracing every kind and shade of colour which can be produced on metals by any means whatever.

The essential portion of the work is treated under three principal divisions, viz.—Chemical Metal-colouring, Electro-chemical Metal-colouring, and Mechanical Metal-colouring, the first of which is by far the largest and most important, while the third, embracing methods which aim at superimposing something on a metal, without necessarily uniting it intimately with the metal, forms but an insignificant part of the whole, and is only included in order to make the work as complete as possible.

It has been considered advisable to include in the introductory portion a brief account of the properties of the ordinary metals and their chemical relations with regard to such elements as oxygen, sulphur, chlorine, etc., as bronzing is essentially a chemical subject and requires

that the metal-colourer should have at least a knowledge of the elementary principles on which the science is based.

The first portion deals with the chemical effects of the atmosphere on metals, the relation of metals to colour, chemical principles and changes, and the nature and object of metal-colouring.

The second portion deals with cleaning, dipping, scratch-brushing, polishing, etc.

The third portion treats of chemical metal-colouring.

The fourth portion is devoted to the subject of Electro-chemical Metal-colouring, embracing the deposition of metals on each other.

The fifth portion refers to the subject of Mechanical Metal-colouring.

The following works among others have been consulted: —Watt's *Dictionary of Chemistry*; *Workshop Receipts*, (Spon); *Die Metallfärbung*, by Buchner; *Bronzage des Métaux et du Platre*, by Lagombe; *Electro-metallurgy*, by Gore; *Electro-deposition*, by Watt; *Electro-deposition*, by Langbein and Brannt; *Colour*, by Church; *Design*, by Dresser.

The author gratefully desires to express his indebtedness to his colleagues, Messrs. Baker and Stansbie, for their care and attention in reading the proof-sheets.

Birmingham Municipal Technical School,
September 1892.

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PART I

INTRODUCTORY

§ 1. The word bronzing is derived from the Italian *Bronzino*—a brown colour, and was originally applied to the browning of metallic articles, but has now come to be applied to the production of all colours alike.

Bronzing is an ancient art, probably dating back to the time when the common metals were first discovered by the human race, and is not confined to any particular nationality. The love of ornament is inherent in human nature, and the peculiar adaptability of base metals to take a kind of beauty when exposed to ordinary atmospheric influences would very soon attract the attention of a lover of the beautiful, and excite a desire to imitate by artificial means the effect produced by the slow continued action of the atmosphere. Every one is charmed with the magnificent display of colours produced in a soap-bubble when its envelope is gradually diminishing in thickness, and in a similar way the film of oxide, which forms on the surface of a piece of bright steel when gradually and slowly heated, calls forth the admiration of the beholder.

The change produced in metals, chiefly by the action of oxygen, would be noted long before any attempt was made to give an explanation of the fact, and ages before the grand discovery of oxygen was made by Priestley. It would further be noted that the air was most effective in producing a colour on metals when in a moist state, and almost inoperative when very dry. At any rate it is a well-known fact at the present time that most metals, when in the massive state, remain perfectly bright and unacted on in dry oxygen or air; but in moist air many of them become slowly oxidised. The coating of oxide first formed frequently protects the metal from more than a superficial oxidation, as is notably the case with lead. On the other hand, some of the ordinarily permanent metals, when in a very finely divided state, such as lead for instance, obtained by the ignition of its tartrate, and iron, as produced by the ignition of Prussian blue, undergo so violent an oxidation that spontaneous combustion results from their mere exposure to air or oxygen. This is in accordance with the well-known fact that various other bodies, which expose a large surface to the action of air or oxygen, become gradually heated through slow oxidation and may finally undergo spontaneous combustion. Greasy cotton waste and woollen refuse are peculiarly liable to this change. Many bodies when heated to redness in air unite with oxygen and give rise to the phenomenon of combustion or burning.

§ 2. Under certain circumstances, oxygen gas acquires a greatly increased chemical activity, together with a peculiar smell. This is observed in the atmosphere during a thunderstorm, or in the vicinity of a machine giving off electric sparks. This modification of oxygen is termed ozone, and like ordinary oxygen is most active as an

oxidising agent when in a moist state. The oxygen evolved by the action of light on plants is largely in the form of ozone. When fresh slices of apple are exposed to the air, ozone is produced; and the same occurs in the processes of fermentation, putrefaction, and decay. The general characters of ozone are those of an oxidising agent. Thus it corrodes organic matter, such as corks and india-rubber; it bleaches most vegetable colours; it oxidises many metallic sulphides to sulphates; changes lower oxides into the higher forms; and not only oxidises, when in a moist state, iron, copper, brass, and bronze, but also silver and mercury with the production of their various oxides. Moist silver is even converted into the state of peroxide. Even dry ozone is absorbed by dry mercury.

The air is a mixture of various gases, viz. nitrogen, oxygen, water vapour, carbonic acid, with minute quantities of ozone, hydroxyl, ammonia, nitrous and nitric acids and hydrocarbons. These gases are not present in any constant ratio, but vary with circumstances. Thus a room with living beings will cause a difference in composition from that of the open air. Or the air of large towns differs from that of the country districts and the sea-coast. Air over marshes contains little or no ozone, and the same remark applies to the air of large towns and inhabited houses. It appears also that the amount of ozone varies with the seasons: it is greatest in spring and least in winter. Ozone is more frequently observed on rainy days than in fine weather; thunderstorms, gales, and hurricanes are generally accompanied by relatively strong manifestations of it. It is highly probable that many so-called ozone manifestations are due to hydroxyl, which is probably in

greater quantity in the air than ozone, and possesses similar oxidising powers.

§ 3. The quantity of *aqueous vapour* in the air varies with the temperature, being greater at warm temperatures than when the air is near the freezing point. The air is seldom saturated with moisture, although in our moist climate saturation is occasionally very nearly attained.

The presence of *carbonic acid* in air is easily proved, and the quantity is greater in large towns than in the country, as any circumstance which interferes with the ready diffusion of the products of respiration and the combustion of fuel will of course tend to increase the relative amount of carbonic acid in the air of a town ; hence during fogs the amount may become relatively very great.

Minute quantities of *ammonia* and *nitrous* and *nitric acids*, as already mentioned, are present in the air. The amount of ammonia which exists mainly as a carbonate varies considerably, but is greatest in towns, owing to the influence of animal life and the constant presence of decaying organic matter in the air. The amount of nitrous and nitric acids is still less than that of ammonia.

Sulphuretted hydrogen is always present in the atmosphere where coal-gas is burnt for heating purposes or for illumination.

All the constituents of atmospheric air, except free nitrogen, have an influence on metals, modifying their colour, and more or less forming compounds with the surface exposed to them. The films of colour thus produced may be due to oxides, carbonates, sulphides, nitrites, nitrates, and possibly hydrocarbonaceous deposits.

§ 4. Metals may, for industrial purposes, be divided into two classes :—Those which are fundamental and

contain only one kind of matter, and those which contain two or more fundamental metals. The fundamental metals, with one or two exceptions, have peculiar tints by which they are distinguished from each other. Thus gold is yellow, copper is red, silver is white, bismuth is reddish-white, lead is bluish-white, etc. But when metals are alloyed together an almost infinite variety of tints may be produced, but always of a subdued tone and quite peculiar to the metallic character.

Hence metals form a class of bodies different from every other form of matter and require special treatment when used for decorative purposes, either in their natural colours or when operated upon so as to produce on the surface the effects produced by the atmosphere or other corroding agents. Nature seems therefore to teach that variety of colour in metals is a most desirable thing, and that it is a laudable action to exalt and intensify the natural chromatic effects, always provided that the colours aimed at are strictly in keeping with the metallic character.

We know that form may exist without colour, but it seldom has any important development without the chromatic adjunct, and history teaches that form alone is incapable of satisfying the instincts of the human mind, for no system of national decoration has ever existed in the absence of colour. Dr. Dresser says, "Mere form, mere light and shade, is pleasing to a certain extent, but it falls far short of what we require, and it is only when we get perfectly proportioned forms in combination with colours harmoniously arranged that we are satisfied." Colour may be applied to almost every inanimate object, and many articles which are now colourless might be coloured with

advantage. Colour lends to bodies a new charm ; it assists in separating parts of an object and thus gives assistance to form, elevating the parts which require prominence, and throwing back the parts which need to be in shadow.

§ 5. It is a common idea that colour is inherent in a body which retains it under all circumstances and conditions. This is not so, for the colour of any object depends entirely on its power of retaining or rejecting certain of the constituent colours of white light. All coloured bodies possess the power of absorbing, or in other words, stopping some of the rays which fall upon them, and reflecting the others. For example, a violet body absorbs all the rays that fall upon it, except the violet, which it reflects ; a green body absorbs all but the green, which it reflects, and so on. A body which absorbs all the rays that fall on it is black ; one which reflects equally all the visible rays is white. A body which absorbs all the rays of light partially but equally is gray. It should be remembered that all bodies, including coloured ones, reflect white light from their immediate surfaces ; it is only the light which penetrates bodies that is, so to speak, sifted and in part reflected so as to give rise to colour.

White light is composed of seven distinct colours, viz. violet, indigo, blue, green, yellow, orange, and red, as may be readily proved by looking at the light through a triangular shaped piece of white glass termed a prism, which has the power of decomposing the white light transmitted through it into its constituent colours. Although white light is composed of the seven primary colours it is not essential that all these colours should combine to form white light. For example, blue and yellow lights when mingled produce white light.

Artists generally recognise only three primary colours, viz. blue, red, and yellow, since they cannot be formed by the admixture of other colours. All other colours except these three may be produced by admixture of these three primary colours. But we must here carefully distinguish between the effects produced by mixing coloured lights and mixing coloured pigments. As already stated, blue and yellow lights produce white light, but a blue and yellow pigment produces a green pigment, because in the latter case the incident light suffers two absorptions—one due to the blue pigment, and the other to the yellow. It is the light which escapes the absorption of both which gives its colour to the mixture. If the blue and yellow pigments used were pure colours — that is, reflected a colour that a prism could not decompose — then their mechanical mixture would be black or gray, for between the two pigments the whole of the light would be absorbed.

But pigments never are pure colours, and the practical effect in the above example is that the blue and yellow both conspire to absorb the red of white light, the yellow absorbs the blue, and the blue the yellow, so that the only part of white light reflected is the green, because neither of the pigments can absorb it. The colours produced by the admixture of two primary colours are termed secondary colours ; the admixture of two secondary colours is called a tertiary colour and so on.

When a light colour is contiguous to a dark colour, the light colour appears lighter than it is, and the dark colour darker ; and different colours juxtaposed become modified as to their hue. Thus when red and green are placed side by side, the red appears redder than it actually is, and the

green greener. When blue and black are in proximity, the blue manifests but little alteration, while the black assumes an orange tint. Any two coloured lights which when mixed produce white light are termed *complementary*; the following pairs of spectrum colours are complementary :—

Red and Greenish-blue,
Orange and Prussian Blue,
Yellow and Indigo Blue,
Greenish-yellow and Violet.

No colour can be persistently viewed by the eye without another being observed. Thus if red be looked at, the eye soon perceives a greenish-blue, and this green is cast on whatever is near. These are termed *subjective* colours. If the eye has been subject for some time to a brilliant white light and then passes into a room only moderately lighted, the room appears dark. Most persons have experienced the effect of passing from a place illuminated by the electric light to one where a sickly-looking gas-flame is burning. In the case of the complementary colours, red and green, above mentioned, the eye having been exposed to red light for a time becomes less sensitive to that colour, and on looking at a white body, such as a sheet of paper, its red constituent is virtually absent, and the complementary colour green appears.

In the same way, if we view a blue, the complementary colour orange or yellow respectively appears; and so we may say that the eye demands white light because that is its natural illuminant, and if only a portion of white light is presented, the eye creates for itself the rest. In the same way coloured shadows are produced. If a strong red light fall on a white screen, and an opaque body be

interposed between the source of light and it, the shadow, as seen when moderately illuminated by a white light, will be green. If the original light be blue, the shadow will be red. All these properties of colour are termed *subjective*, because they do not express external facts but depend on the condition of the eye.

§ 6. Another cause of colour is what is known as *interference*. If a stone be thrown into water, a circular wave is produced, and if a second stone be thrown into the same water, a second wave will be produced, which will influence the first. If the two stones fall into the water at precisely the same time and place, the two waves will beat in unison, and the amount of disturbance in the water will be double what it would have been if only one stone had been thrown in. If the second stone had been thrown into the water exactly a wave-length behind the first, the same thing would happen, for the first crest of the second wave would coincide in point of time with the second crest of the first wave and produce perfect unison. But if the second stone were thrown into the water exactly half a wave-length behind the first, the crest of one wave would be opposed by the depression of the other; and if the height of each wave be the same, the motion of the water will be destroyed.

The same action occurs in light which is propagated by wave-motion in a similar way to that in water. Take a soap-bubble for illustration. When light impinges on the soap film, part of it is reflected from the exterior surface, and part enters the film and is reflected from the interior surface. This latter portion has to traverse the thickness of the film twice, and is therefore retarded with respect to the former, so that the two sets of waves interfere with

each other and produce a coloured light in the place of white light. If two waves are equal and there is exactly half a wave-length difference between them, they will destroy each other, and therefore extinguish the light.

But white light is composed of several colours, each of which has a different wave-length, so that if the white light which enters a soap-bubble is resolved into its constituent colours, some may so interfere as to destroy each other, but some will remain unaffected, the longer waves requiring a greater thickness of film than the shorter to produce their extinction; hence the alteration in the colours of a soap-bubble as its film gradually alters in thickness. In this way we may account for the iridescence of oil upon water, of steel when being tempered, the hues of some insects' wings, and the colours of thin plates or films generally.

When light passes from one transparent medium to another it is bent or *refracted*, except at certain angles when it may be totally reflected. If a surface contains a number of fine lines very close together, the light reflected from the different portions will be in interference, and variegated colours will result. In this way it is supposed that the magnificent chromatic display often observed in mother-of-pearl is due to reflection from its striated surface. The colouring of metals and many other objects may often be traced to the same cause.

§ 7. When contrasted musical notes give a pleasing sound we call the result harmony. In the same way there are certain contrasted colours which produce an agreeable impression on the eye, and these may also be said to harmonise. Those colours which most perfectly harmonise improve one another to the utmost, and this is effected by a combina-

tion of the three primary colours, red, blue, and yellow, either pure or in combination with each other. Red and green harmonise, because green is a secondary colour consisting of blue and yellow. Blue and orange, yellow and purple, respectively are in harmony, for in each case the three primary colours are present. On the other hand, there are combinations of colour which are perfectly hideous, producing the completest discord, although it is true that the rarest harmonies frequently lie close on the verge of discord.

It has been already stated that colours are modified in tone by the proximity of other different colours, so that the nature of the light by which a coloured body is viewed will influence the effect on the retina of the eye. For example, by ordinary gaslight blue becomes darker, red brighter, and yellow lighter. By this artificial light a pure yellow appears lighter than white itself, when viewed in contrast with certain other colours. In this way highly polished brass is often mistaken for silver. At twilight blue appears much lighter than it is, red much darker, and yellow slightly darker.

Colours also have the power of influencing the beholder in various ways; thus blue looks cold and appears to recede from the eye. Red is a warm colour and exciting; it remains stationary as to distance. Yellow is the colour most nearly allied to white light; it appears to advance to the spectator. By certain combinations colour may be made to cheer or sadden; to convey the notion of purity, richness, or poverty, and in fact affect the mind in much the same way as does music.

The following principles with regard to colour in design are given by Dr. Dresser:—"(1) When a colour is placed

on a gold ground it should be outlined by a darker shade of its own colour. (2) When a gold ornament falls on a coloured ground, it should be outlined with black. (3) When an ornament falls on a ground which is in direct harmony with it, it must be outlined with a lighter tint of its own colour. Thus, when a red ornament falls on a green ground, the ornament must be outlined with a lighter red. (4) When the ornament and the ground are in two tints of the same colour, if the ornament is darker than the ground, it will require outlining with a still darker tint of the same colour, but if lighter than the ground, no outline will be required." There are three colours which are neutral with regard to colour, viz. gold, black, and white, and these may be employed to separate colours where such separation is necessary or desirable.

§ 8. It has already been said that metals form a class of bodies quite peculiar to themselves, and differ from every other known substance. They therefore should have such special treatment in any system of colouring as will enable the metallic character still to be evident, or at least to be suggested. Anything which completely hides the metallic nature and represents it as something which it is not, may be very ingenious and display a considerable amount of manipulative skill, but it is a spurious form of art. In my opinion nothing should be added to any form of metal for the purposes of metal-colouring except what is capable of becoming a part of itself. For this reason paint in any form is not admissible, as it forms a layer of matter, non-metallic in character, simply superposed on the metal and not in any sense uniting with it to form a compound effect.

In the same category are lacquers and varnishes of all

kinds, however beautifully they may be coloured. It is true that lacquers and varnishes are very useful and even necessary to preserve many metals from the corrosive action of the atmosphere and other agencies to which they are subjected, but they should only be used when absolutely necessary, and then only the uncoloured and transparent variety should be employed.

What a disappointment it is to see some really meritorious brass or bronze work highly lacquered so as to shine like a French-polished piece of furniture instead of having the subdued lustre peculiar to the metallic character. It is a grand and beautiful thing to imitate beautiful things, but it is degrading to true taste to make a metal look like wood or glass and *vice versa*. Let us beautify metals so as to present as great a variety of charms to the beholder as possible, but never make the metal to lose all semblance of its real nature.

It is a good sign that at the present time the national taste is setting in in the direction of plain metal work. Brass is finished as brass, iron as iron, copper as copper, showing the repugnance felt by a people advancing in artistic taste to the shams and paints and varnishes which a past generation endured. One occasionally sees in private and public rooms metal picture rails painted in various tints to match the wall decoration or the furniture, with nothing whatever to distinguish between the material of which the rail is composed and that of the plaster wall. This is utterly wrong in principle; it may be called harmonious blending of colours, tasteful decoration, and so on but it is a perversion of true art and should never be encouraged. Have we not metals of various shades which lend themselves more perfectly to decoration than any

paint superimposed upon them can do? Moreover, we have yellow gold, and white tin and silver, which, being quite neutral as to colour, will always lend themselves perfectly to metallic decoration.

It is truly marvellous to see what effects may be produced by certain pickling solutions on impure metals, compared with similar effects on the same metal when in a pure state, and this is often true when the foreign matter is present in such minute quantity as to seem to a non-scientific person infinitesimal and unworthy of consideration. Yet a minute quantity of one metal can change the whole of another metal in which it is hidden, causing it to behave in a different way in relation to light, and consequently to possess a colour different to that which it would have when pure. That various shades of colour may be produced in metals by alloying them together in various proportions is well known. Take, for example, a mass of red copper and an equal weight of gray antimony; the union of the two by fusion produces a beautiful violet alloy. The same colour may be obtained by depositing copper on an article, such as a brass ash-tray, and then immersing the same for a few seconds in a solution containing antimony. The thin film of antimony thus deposited gives to the surface the well-known violet tint characteristic of the above-mentioned alloy, termed *Regulus of Venus*. This alloy is too brittle to work, but the colour may be imparted to base metals in the manner indicated above.

The colouring power of metals in alloys is very variable, as shown by the following table by Ledebur :—

Tin	Zinc
Nickel	Lead
Aluminium	Platinum
Manganese	Silver
Iron	Gold
Copper	...

Each metal in the above series has a greater decolourising action than the metal following it. Thus, the colour of the last members is concealed by comparatively small amounts of the first.

That tin and nickel readily whiten copper in gun metal and nickel-silver respectively is well known. On the other hand, gray zinc requires to be in considerable excess in brass before the yellow tint characteristic of that alloy is completely destroyed.

§ 9. The Japanese, however, are the real authorities to whom we must turn for examples of the highest kind of coloration in metals. They combine the most perfect artistic taste with marvellous manipulative skill in executing any design their imagination may suggest. In certain branches they are inimitable, and as colourists they are almost perfect. Their commonest works generally contain a bit of good colouring, and their best efforts are marvels of harmony. Their colours are usually warm, simple, and quiet, but always effective. Even the bloom on the surface of fruit is very faithfully reproduced by them. These facts are all the more remarkable when we consider how impure their ordinary commercial metals are compared with ours, and how infinitely we excel the Japanese in the knowledge of metals from a scientific standpoint.

It is true that impure metals are sometimes better adapted for producing varieties of colour on metals by means of

bronzing solutions; but we, by means of our great army of analysts and scientific men, can ascertain the exact composition of the alloys they use, and with our richer stores of mineral wealth and metallurgical knowledge can produce any variation we choose in the composition of alloys, as every known metal, if not existing in the British Isles, is procurable by us. If complexity of composition is the secret of success, we have the knowledge and the skill to make such complexes.

But the same cannot be said of our art knowledge. It is true there are individual Englishmen who are the equals of the greatest artists of any other nation; but there is not among us the same desire to cultivate that artistic taste generally which seems to pervade every section of the community in Japan, high and low, rich and poor, and with regard to art metal work we are vastly inferior as a nation. But if we cannot equal them we can strive towards greater perfection, and for the present be content to imitate the admirable skill attained by this truly artistic people.

One sad feature with regard to the closer European contact with Japan is said to be a deterioration of Japanese art work to a lamentable extent. Contact with Europeans, and especially with Englishmen, causes a much greater demand for Japanese wares, so that quantity is being produced, it is feared, at the expense of quality. We cavil about prices, and by thus creating a demand for inferior work we raise the price even of that which is comparatively bad, and soon we shall have to pay for inferior wares a price for which superior articles could formerly be obtained.

Happily at present nothing from Japan and India, of native workmanship, is utterly bad. Inharmonious colour-

ing does not appear to be produced by these nations. Sir Frederick Leighton, in his Address to the Art Congress at Liverpool, said: "Our complaint with respect to the great majority of Englishmen is that the appreciation of art is blunt, superficial, desultory, and spasmodic; that our countrymen have no adequate perception of the place of art as an element of national greatness; that they do not count its achievements among the grounds of their national pride; that they do not appreciate its vital importance in the present day to certain branches of national prosperity; that while what is excellent receives from them honour and recognition, what is ignoble and hideous is not detested by them; that the æsthetic consciousness is not with them a living force, impelling them towards the beautiful and rebelling against the unsightly."

FUNDAMENTAL CHEMICAL RELATIONS

§ 10. Before proceeding with the description of the production of the various colours produced on bodies by different bronzes, it will be necessary to give a general idea of the physical and chemical properties of the metals, and to explain the nature of chemical change which plays such an important part in bronzing.

With about seventy exceptions all known substances, by various chemical processes, may be decomposed, and are therefore termed *chemical compounds*; while the seventy known bodies which have never been resolved into simpler parts are termed *chemical elements*. Of the latter more than three-fourths possess metallic properties, and are distinguished by the name of *metals*, in contradistinction to the remainder which are termed *non-metals*.

The chemical elements possess almost every shade of physical character, and if we include the infinite variety of metals which can be produced by the process of alloying, the significance of this statement is still more marked. Among elementary substances we have oxygen, nitrogen, hydrogen, chlorine, and fluorine, which are gases under all ordinary conditions. Bromine and mercury are liquids.

With regard to the solids it may be stated that some are readily volatile, such as iodine and arsenic, some easily fusible, such as phosphorus, and some which require the

very highest temperatures to effect their fusion, such as platinum. Hydrogen is the lightest and osmium the heaviest of all known bodies. Many elements occur in nature in the free state, such as oxygen, nitrogen, sulphur, gold, silver, copper, etc.; but by far the larger portion only exist in combination with other bodies, and those which occur in the free state, with three or four exceptions, only do so in comparatively small quantities.

The elements are very unequally distributed throughout nature, some being exceedingly abundant, others only occurring in the minutest quantities in any one place. One-half the solid crust of the globe, eight-ninths of water, and one-fifth of the atmosphere is the element oxygen. Moreover, many other elements are most frequently found in combination with oxygen, so that this element may be considered as the cement by which the elementary parts of the world are held together. Of the known elements, thirteen alone make up $\frac{99}{100}$ of the whole mass of the earth.

The ultimate particles or "atoms" which compose any element differ in weight from the atoms of any other element, and the relative weight compared with hydrogen is termed the "atomic weight." The atoms are usually represented by symbols. The following table gives the chemical elements with their symbols, atomic weights, and specific gravities :—

METALS.

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Aluminium	Al	27	2·56
Antimony	Sb	120	6·72
Arsenic	As	75	5·67
Barium	Ba	137	3·75
Bismuth	Bi	207·5	9·8
Cadmium	Cd	112	8·6
Cæsium	Cs	133	...
Calcium	Ca	40	1·58
Cerium	Ce	141	6·68
Chromium	Cr	52	6·8
Cobalt	Co	58·6	8·5
Copper	Cu	63·2	8·8
Didymium	Di	95	6·5
Erbium	E	112·6	...
Glucinum	Gl	9	2
Gold	Au	196·2	19·32
Indium	In	113·4	7·4
Iridium	Ir	192·5	22·4
Iron	Fe	56	7·86
Lanthanium	La	138·5	6·2
Lead	Pb	206·4	11·37
Lithium	Li	7	·58
Magnesium	Mg	24	1·74
Manganese	Mn	55	8
Mercury	Hg	200	13·59
Molybdenum	Mo	96	8·6
Nickel	Ni	58·6	8·8
Niobium	Nb	94	6·27
Osmium	Os	195	22·48
Palladium	Pd	106·2	11·5
Platinum	Pt	194·3	21·5
Potassium	K	39·1	·87
Rhodium	Rh	104	12·1
Rubidium	Rb	85·2	1·52
Ruthenium	Ru	103·5	12·26
Silver	Ag	107·6	10·5
Sodium	Na	23	·97

METALS—*Continued.*

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Strontium	Sr	87·2	2·54
Tantalum	Ta	182	10·78
Thallium	Tl	203·5	11·9
Thorium	Th	232	11·1
Tin	Sn	117·4	7·3
Titanium	Ti	48	...
Tungsten	W	184	19·1
Uranium	U	240	18·7
Vanadium	V	51	5·5
Yttrium	Y	61·7	...
Zinc	Zn	65·2	7·15
Zirconium	Zr	90·4	4·15

NON-METALS.

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Boron	B	11	2·68
Bromine	Br	80	2·96
Carbon (Graphite)	...	...	2·2
Carbon	C	12	...
Carbon (Diamond)	...	...	3·5
Chlorine	Cl	35·5	...
Fluorine	F	19	...
Hydrogen	H	1	...
Iodine	I	127	4·95
Nitrogen	N	14	...
Oxygen	O	16	...
Phosphorus	P	31	1·8–2·1
Selenium	Se	79·5	4·28–4·8
Silicon	Si	28·1	2·49
Sulphur	S	32	1·97–2·07
Tellurium	Te	126·3	6·25

§ 11. **Molecules.**—Every body, whatever its substance may be, is formed by the assemblage of minute particles of the same kind, which cannot be further subdivided without destroying the identity of the substance. Thus a lump of sugar is an aggregate of minute particles of sugar, and if the sugar be burnt, these particles will be further subdivided; but the sugar will be changed into new substances. The smallest particles of any substance which can exist by themselves we call Molecules. So long as the identity of a substance is preserved its molecules remain undivided; but when, by some chemical change, its identity is lost and new substances are formed, the molecules are broken up into still smaller particles which are termed *atoms*. Indeed, this division of the molecules is the very essence of a chemical change, and the atom may be defined as the smallest mass of an element that can exist in any molecule.

§ 12. **Chemical Nomenclature.**—There are several systems in use of naming chemical compounds, but no one of these is rigidly followed. Previous to 1787 no general rule was followed, and even now many of the old empirical names are more extensively used than the more modern ones. Thus we still speak of *oil of vitriol*, *calomel*, *corrosive sublimate*, *saltpetre*, *common salt*, *borax*, *cream of tartar*, *Epsom salts*, etc. The simplest of the nomenclatures—for compounds containing two elements—is that of writing the name of the metal first and the non-metal or least metallic element last, giving it the termination *ide*. When two non-metals unite the one which is least like a metal is written last.

In addition to this, Greek prefixes are in common use, such as *mono*, *di*, *tri*, *tetr*, etc., to indicate the number of

atoms present. Thus, carbon dioxide, CO_2, carbon monoxide, CO. Another system consists of making the metal terminate in *ic* or *ous*. That compound which contains the greater proportion of the non-metallic constituent is distinguished by the suffix *ic*, and that containing the smaller is *ous*. The following list will illustrate these points :—

Name.	Name.	Name.	Formula.
Iron oxide	Ferrous oxide	Iron protoxide	FeO
Iron trioxide	Ferric oxide	Iron sesquioxide	Fe_2O_3
Iron tetroxide	Triferric tetroxide	Black oxide of iron	Fe_3O_4
Manganese oxide	Manganous oxide	Manganese protoxide	MnO
Manganese dioxide	Manganic oxide	Manganese peroxide	MnO_2
Aluminium oxide	Aluminic oxide	Alumina	Al_2O_3
Calcium oxide	Calcic oxide	Lime	CaO
Magnesium oxide	Magnesic oxide	Magnesia	MgO
Titanium dioxide	Titanic oxide	Titanic acid	TiO_2
Carbon monoxide	Carbonic oxide	...	CO
Carbon dioxide	...	Carbonic acid	CO_2
Silicon dioxide	Silicic oxide	Silica	SiO_2
Phosphorus pentoxide	Phosphoric oxide	Phosphoric acid	P_2O_5
Sulphur dioxide	Sulphurous oxide	Sulphurous acid	SO_2
Sulphur trioxide	Sulphuric oxide	Sulphuric acid	SO_3

When three or more elements—one being a metal and another oxygen—are combined together, the name of the second is made to end in "ate." In the following list a few compounds are given to illustrate this, but it should be observed that the order of placing the symbols is immaterial :—

Name.	Name.	Formulæ.
Lead acetate	Plumbic acetate	$Pb(C_2H_3O_2)$ or $PbO_2(C_2H_3O)_2$
Iron sulphate	Ferrous sulphate	$FeSO_4$ or $FeO.SO_3$
Calcium carbonate	Carbonate of lime	$CaCO_3$ or $CaO.CO_2$
Silver nitrate	Argentic nitrate	$AgNO_3$
Potassium chlorate	Potassic chlorate	$KClO_3$

§ 13. **Equations.**—When two or more elements unite to form a compound, or two compounds unite to form a more complex compound, the change may be represented by a chemical equation, thus—

Cu	+	O	=	CuO
Copper.		Oxygen.		Cupric oxide.
63·2		16		79·2
CuO	+	CO_2	=	$CuCO_3$
Cupric oxide.		Carbonic acid.		Copper carbonate.

Any chemical change may be so represented, the bodies taking part in the change being placed on the left-hand side of the sign of equality "=," and the bodies formed after the change on the right-hand side.

The quantities involved in any such change can be seen at a glance, since the symbol of an element represents a definite weight, given in the table, p. 20, as the atomic weight. Thus, in the first equation 63·2 parts of copper unite with 16 parts of oxygen to form 79·2 parts of cupric oxide.

When a chemical change occurs, the production or absorption of heat is the result, the former by the union of elements or compounds, the latter by the forcible separation of the constituents of a compound. When the increase in

temperature produced is considerable, it is usual to speak of the change as combustion; thus, carbon combines with oxygen to produce carbonic acid and generates intense heat.

C	+	2O	=	CO_2
Carbon.		Oxygen.		Carbonic acid.

In common language it is said to burn, and the burning of fuel is simply the result of chemical combination.

§ 14. When substances combine with oxygen they are said to be "oxidised," and the substance which imparts the oxygen is termed an oxidising agent. Conversely, substances which remove oxygen from a body are termed reducing agents. The following lists give some examples of both kinds:—

Oxidising Agents.	*Reducing Agents.*
Oxygen (O).	Carbon (C).
Air (O and N).	Carbonic oxide (CO).
Iron tetroxide (Fe_3O_4).	Hydrogen (H).
Manganese dioxide MnO_2.	Compounds of carbon and hydrogen, such as coal-gas.
Slags containing the above or similar oxides.	All fuels.
Carbonic acid (CO_2).	Sometimes metals.
Water (H_2O).	

Examples of Oxidation.

$3PbO$	+	O	=	Pb_3O_4		
Lead oxide.		Oxygen.		Red lead.		
$3FeCO_3$	+	O	=	Fe_3O_4	+	$3CO_2$
Iron carbonate.		Oxygen.		Iron tetroxide.		Carbonic acid.
$3FeO$	+	CO_2	=	Fe_3O_4	+	CO
Iron oxide.		Carbonic acid.		Iron tetroxide.		Carbonic oxide.

Examples of Reduction.

$2PbO$	+	C	=	CO_2	+	Pb_2
Lead oxide.		Carbon.		Carbonic acid.		Lead.

Examples of Reduction.—Continued.

Fe_2O_3	+	6H	=	2Fe	+	$3H_2O$
Ferric oxide.		Hydrogen.		Iron.		Water.
ZnO	+	CO	=	Zn	+	CO_2
Zinc oxide.		Carbonic oxide.		Zinc.		Carbonic acid.
Fe_2O_3	+	CO	=	2FeO	+	CO_2
Ferric oxide.		Carbonic oxide.		Ferrous oxide.		Carbonic acid.
PbS	+	Fe	=	Pb	+	FeS
Lead sulphide.		Iron.		Lead.		Ferrous sulphide.

It will be obvious that in the cases of oxidation and reduction the change may be partial or complete. Thus, iron is completely oxidised when converted into Fe_2O_3, and oxide of iron is completely reduced when all the iron is brought to the metallic state.

The following is a short description of the chief substances mentioned in the present part, and which are subsequently alluded to :—

§ 15. **Oxygen** (O).—This is the most abundant element, forming probably one-half the solid crust of the earth, eight-ninths of all water, and about 21 per cent by volume of the air. It is necessary for life and all ordinary processes of combustion. In the air it is a gas, but its compounds are chiefly solid or liquid. Its oxidising action has been already mentioned. It is the chief supporter of combustion, that is, it forms the active medium in which bodies burn.

Oxides, as the compounds of oxygen with other elements are termed, may be roughly divided into two groups. 1°. Those which have an acid character, chiefly oxides of the non-metals, and often termed acids, such as carbonic acid CO_2 and silica SiO_2. 2°. Those of a basic character, chiefly oxides of the metals, which are termed bases. These two classes are opposite in character, and when united in equivalent proportions, generally neutralise each

other, forming what are termed "neutral" bodies, which do not possess the characteristic properties of either kind. Thus silica SiO_2 will neutralise oxide of iron FeO, forming a silicate, which is neither acid nor basic. If any compound contain an excess of acid or base, it is classified either as an acid or as a basic substance, according to the kind which predominates. Thus, $3FeO.SiO_2$ is a basic silicate, and $FeO.SiO_2$ an acid silicate, because in the former there is more FeO than is required to neutralise the acid SiO_2, and in the latter less than is necessary for this purpose.

§ 16. **Hydrogen** (H) is chiefly found in nature in combination with oxygen, forming water H_2O, which contains one-ninth its weight of hydrogen. It differs from other non-metals in not generally uniting with metals to form compounds, but metals such as palladium and iron absorb it in large quantities, when it is said to be occluded. It burns in air or in pure oxygen, forming water, and evolving great heat—

$$2H + O = H_2O.$$

It is a constituent of wood, peat, coal, and coal-gas, part of it probably existing in these bodies as water; and in combination with carbon it forms what are termed hydrocarbons, such as marsh-gas CH_4, and olefiant-gas C_2H_4. When the latter are burnt the hydrogen forms water, thus—

CH_4	+	$4O$	=	CO_2	+	$2H_2O$
Marsh-gas.		Oxygen.		Carbonic acid.		Water.
C_2H_4	+	$6O$	=	$2CO_2$	+	$2H_2O$
Olefiant-gas.		Oxygen.		Carbonic acid.		Water.

On account of the readiness of hydrogen to unite with oxygen it is used as a reducing agent and thus removes the oxygen from a compound containing it.

§ 17. **Nitrogen** (N) forms about 79 per cent by volume

of the air, its chief function being to modify the active properties of oxygen. It neither burns nor supports combustion, so that the nitrogen which enters a furnace, for the most part, comes out unchanged, thus robbing it of a large amount of heat, without contributing any itself.

Air is chiefly a mixture of oxygen and nitrogen along with small quantities of water and carbonic acid. Omitting the latter, its composition may roughly be taken as—

	By Volume.		By Weight.
N	79	N	77
O	21	O	23
	100		100

A ton of air thus contains about 515 lbs. of oxygen. Air resembles oxygen in its properties, but is less active on account of the inactive nitrogen.

§ 18. **Silicon** (Si).—This non-metal is a grayish-black substance. It is generally present in iron and a few other metals, and supposed to exist, like carbon, in the "free" and in the "combined" state. It is of little importance as an element, but in combination it forms about one-fourth of the earth's crust. It burns in oxygen, forming silica, thus—

Si	+	2O	=	SiO_2
Silicon.		Oxygen.		Silica.

Silica (SiO_2) plays a prominent part in the reduction of metals from their ores, being the chief slag-forming substance. It exists largely as sand, and in combination with "bases" it forms silicates. The various slags are chiefly combinations of SiO_2 with alumina Al_2O_3, lime CaO, and other metallic oxides which fuse at high temperatures. Uncombined silica is practically infusible.

§ 19. **Carbon** (C).—This non-metal is an essential con-

stituent of all living matter, and of all ordinary fuels, such as coal. It exists in the free state as the diamond, and as graphite or black-lead. In the latter form it is used in the manufacture of crucibles, etc., because of its infusibility, and its non-tendency to form fusible slags with acid or basic substances. It will burn away in contact with air, but will not melt or vaporise. It exists in pig-iron and steel in the free and in the combined state. Part of the free carbon of pig-iron sometimes rises to the surface of the molten mass when allowed to stand, and is known as "kish." Charcoal and coke are almost entirely composed of carbon, with a little earthy matter, which is left as ash when the carbon is burnt. Either form of carbon will burn in oxygen, forming oxides. When carbon is strongly heated in the presence of steam the latter is decomposed and the carbon oxidised, thus—

C	+	H_2O	=	H_2	+	CO
Carbon.		Water.		Hydrogen.		Carbonic oxide.
3C	+	$2H_2O$	=	CH_4	+	2CO
Carbon.		Water.		Marsh-gas.		Carbonic oxide.

Carbon dioxide or Carbonic acid (CO_2) is a gas about $1\frac{1}{2}$ times the weight of air, and is formed when carbon is burned in oxygen or in a free supply of air, thus—

C	+	2O	=	CO_2
Carbon.		Oxygen.		Carbonic acid.

Also when carbonic oxide is burned in air or oxygen, thus—

CO	+	O	=	CO_2
Carbonic oxide.		Oxygen.		Carbonic acid.

If carbon dioxide is brought in contact with red-hot carbon, it takes up some of the latter, forming twice its own volume of carbonic oxide (CO), thus—

CO_2	+	C	=	2CO
Carbonic acid.		Carbon.		Carbonic oxide.

In this case carbonic acid is oxidising. CO_2 is not poisonous, but it will not support life or ordinary combustion.

Carbon monoxide or Carbonic oxide (CO) is a colourless gas, about the same weight as air, extremely poisonous, and burns in air or oxygen with a blue flame producing carbonic acid, and evolving considerable heat. The combustible gas formed in gas-producers is chiefly carbonic oxide. It is a powerful reducing agent, probably the chief agent in reducing oxide of iron in the blast-furnace, and zinc oxide in zinc muffles. At high temperatures CO is decomposed, especially in the presence of other bodies, such as iron, which combine with carbon.

$$\underset{\text{Carbonic oxide.}}{2CO} = \underset{\text{Carbon.}}{C} + \underset{\text{Carbonic acid.}}{CO_2}$$

This is probably the case in the blast-furnace, and in the cementation process for steel.

§ 20. **Phosphorus** (P).—This non-metal is generally a waxy-looking crystalline solid, which readily melts and vaporises. It is highly inflammable in air, forming a white cloud of phosphorus pentoxide P_2O_5, also called phosphoric acid. The red variety of phosphorus is much less inflammable than the above. It combines with oxygen in two proportions, forming oxides of phosphorus. One of these oxides unites with bases to form compounds termed phosphates. It probably exists in metals as an element, but in slags as a phosphate.

§ 21. **Sulphur** (S) is a non-metal, and solid at ordinary temperatures. It readily melts and vaporises, and unites with metals forming sulphides, such as ferrous sulphide FeS. With oxygen it forms oxides, viz. sulphur dioxide SO_2, and sulphur trioxide SO_3.

§ 22. **Chlorine.**—This element exists in nature mainly

in combination with sodium, calcium, potassium, magnesium, etc. At ordinary temperatures and pressures chlorine is a greenish-yellow gas, having a pungent and irritating smell, but by great pressure may be liquefied to a dark greenish-yellow liquid, and at low temperatures may be solidified. It is readily soluble in water. It is an active chemical agent, and combines with most metals, forming a class of bodies termed chlorides. Indirectly it acts as a powerful oxidising agent, and is thus used in bleaching and as a disinfectant. In combination with hydrogen it forms hydrochloric acid HCl.

PROPERTIES OF THE METALS

Noble Metals—Gold, Platinum, Silver

§ 23. **Gold** is usually found in the metallic state in nature (generally associated with silver, and sometimes with copper, iron, and platinum). It is often found in ores of lead, zinc, iron, and copper. Gold is a yellow metal, with a brilliant lustre; it exceeds all others with regard to malleability and ductility; its specific gravity is 19·32; its melting point about 1050° C.; and it is only volatile at very high temperatures. It is almost as soft as lead, and can be welded by pressure in the cold; it is one of the best conductors of heat and electricity.

Gold does not oxidise in air, nor is it acted on by any single acid except selenic, but is dissolved by substances like aqua regia which yield chlorine. Chlorine gas unites directly with gold to form gold chloride $AuCl_3$. It is unacted upon by sulphur or its compounds, so that gold exposed to sulphurous fumes does not become tarnished like silver under similar circumstances. Pure gold is too

soft for general use, so that it is usually alloyed with silver and copper, which harden it, without seriously impairing its malleability and ductility. Antimony, arsenic, and lead are most injurious substances in gold, even when present in minute quantities.

Platinum is a white metal, with a brilliant lustre; highly malleable and ductile; as soft as silver, and can readily be welded; it is very tenacious, being only exceeded in this respect by iron and copper among the elementary metals; it only melts at the highest temperatures, such as those of the oxy-hydrogen flame, and the electric arc. It does not oxidise at any temperature, and resists the action of all single acids, its best solvent being aqua regia. It is one of the heaviest metals, having a specific gravity of 21·5. Like silver it absorbs oxygen when melted, giving it out again on cooling, causing the mass to spit. It absorbs considerable quantities of hydrogen and other gases when strongly heated with them, especially the spongy variety called platinum black; if this substance be introduced into a mixture of oxygen and hydrogen it causes them to combine, with the development of great heat.

Platinum occurs in nature, like gold, in the metallic state, in the form of grains or nuggets, and is often associated with iron, copper, gold, silver, and several rare metals.

Silver is remarkable for its whiteness and brilliant lustre, although when precipitated from its solutions it often forms a gray powder; it is harder than gold, but softer than copper, the relative hardness being as 4 : 5 : 7·2. Silver is extremely malleable and ductile, with a tenacity of about 14 tons per square inch; its specific gravity is 10·5, which may be slightly increased by the operations of coining, rolling, hammering, etc.; it melts below 1000°

C.; is one of the best conductors of heat and electricity; is volatile at high temperatures, and at the temperature of the electric arc it may be boiled and distilled. When heated in a current of hydrogen it volatilises at 1330° C. It does not oxidise when heated in air, but molten silver mechanically absorbs oxygen and emits it on solidifying; this is termed "spitting." Silver in a finely divided state is oxidised when heated with certain metallic oxides, such as cupric oxide, manganese dioxide, red lead, etc., these bodies being reduced to lower oxides. Silver is soluble in nitric and sulphuric acids. Silver unites readily with sulphur when heated, forming silver sulphide Ag_2S, which is a dark gray, crystalline body, with feeble lustre; somewhat soft and malleable. When heated in air it does not form oxide or sulphate, like most other metallic sulphides, and at a red heat is decomposed into metallic silver and sulphur. Dilute hydrochloric acid has no action on silver sulphide, but the strong acid attacks it. Lead, copper, or iron decomposes it when the two bodies are fused together. When silver sulphide is heated with common salt, in the presence of moist air, silver chloride is formed.

Silver and all its salts dissolve in sodium thiosulphate, forming a soluble double thiosulphate ($Na_2S_2O_3 + Ag_2S_2O_3$), when the sodium salt is in excess. Silver combines directly with chlorine to form silver chloride AgCl. The same substance is formed by adding hydrochloric acid, or a solution of common salt to a solution containing silver, when AgCl is precipitated as a white powder; if, however, a large excess of strong salt solution be used the AgCl is dissolved, a double salt being formed thus—

$$AgNO_3 + NaCl = AgCl + NaNO_3$$
$$AgCl + NaCl = (AgCl, NaCl).$$

Silver chloride fuses at a low red heat to a yellow liquid and readily volatilises at a strong red heat. It is insoluble in acids, but soluble in ammonia, sodium chloride, sodium thiosulphate, and potassium cyanide. It may be reduced by hydrogen, carbonate of soda, zinc, iron, and several other metals, and partially by sulphur. It unites with oxide of lead in all proportions, and partially so with sulphide of lead and some other sulphides.

Silver occurs in nature in the metallic state; as sulphide in silver glance, which is often associated with the sulphides of lead, antimony, and iron; as bromide and iodide; as chloride in horn silver; in many lead, zinc, and copper ores; and sometimes in iron pyrites.

Silver is too soft to be worked by itself for most purposes, pure silver being only used in special cases, where the presence of another metal would exert an injurious effect. In most cases silver is alloyed with copper, and occasionally with other metals, as in silver solders.

Copper Group—Copper, Mercury, Lead, and Bismuth

§ 24. **Copper** has a red colour; is highly malleable, ductile, tough, and tenacious; it melts at about 1050° C., is not sensibly volatile, except at very high temperatures; its specific gravity is 8·8, which may be slightly increased by hammering and rolling. Copper is one of the best conductors of heat and electricity, but this property is considerably interfered with by the presence of small traces of

impurities. When a bar of pure copper is freshly broken it exhibits a fibrous silky fracture of a light salmon colour. It readily unites with oxygen at a red heat, forming one or both of the two oxides, known respectively as black and red oxide, in virtue of their colour. The red or cuprous oxide is highly basic, and unites with acid substances, such as silica, forming copper salts. Cuprous oxide is soluble in molten copper, making it dry in appearance and brittle in character. This may be remedied by remelting the copper with a little charcoal, and stirring with a pole of green wood. Commercial or tough-pitch copper is never pure, but the impurities are neutralised by the presence of a little oxygen. If the poling referred to above be continued too far, the neutralising oxygen is removed and the other impurities present act on the copper prejudicially, making it brittle. The copper is then said to be over-poled.

Copper unites directly with sulphur when the two bodies are heated together forming cuprous sulphide, which is of a dark bluish-gray colour, shows a finely granular fractured surface when broken, and has a metallic lustre.

Phosphorus is highly injurious to copper when allowed to remain in it, but a small quantity may, under certain circumstances, exert a refining influence, provided the whole of it is afterwards removed.

The element silicon, when reduced from sand by the action of carbon, unites with copper, making it much harder, and causing it somewhat to resemble gun-metal in colour, but diminishes its toughness and malleability.

Lead, arsenic, and antimony have a very injurious action on copper, making it hard, brittle, and cold-short.

The common impurities in copper are iron, arsenic, antimony, and cuprous oxide; sometimes tin, bismuth, sulphur, lead, nickel, and cobalt are present. The varieties of commercial copper are—rosette or Japan copper, the surface of which presents a peculiar red colour, due to a coating of oxide, formed by throwing water on the surface of the metal while in a heated state. Bean-shot and feathered-shot copper, which are obtained in the form of globules and flakes respectively, by running the metal into hot or cold water. Tough-cake is a variety cast into rectangular slabs, convenient for rolling, etc. Best-selected is the name applied to the purest variety of commercial copper, special care being taken to free it from sulphur, arsenic, antimony, and iron. Russian-copper generally contains traces of iron, but is otherwise very pure. Chili-bars. This variety, as imported into this country, is prepared in bars weighing about 200 lbs. each; the copper being in a raw state, requires to be refined before it is ready for use.

Mercury.—This is the only one of the useful metals which is liquid at ordinary temperatures; it is also called quicksilver, and has been known from the most remote times. It has a silver-white colour with a brilliant lustre; is devoid of taste or odour when pure; at a temperature of 360° C. it boils, and at − 39·4° C. it solidifies, forming a soft white malleable mass, exhibiting a granular structure on the freshly fractured surface. It has a high and fairly regular coefficient of expansion for heat, which renders it suitable for thermometers and similar instruments; its specific heat is ·0332, and its density at 4° C. is 13·59. Liquid mercury does not oxidise in air, except near its boiling point, which forms a ready means of detecting the

presence of base metals, such as lead and antimony, added as adulterations, or present as impurities. Impure mercury, when exposed to air or oxygen, becomes coated with a gray film, due to the oxidation of the impurities. At its boiling point mercury is slowly oxidised to mercuric oxide HgO. It combines directly with sulphur, forming an important compound, mercuric sulphide or vermilion HgS.

Mercury unites with most metals forming "amalgams," some of which are liquid, others semi-liquid, and some solid. The solid amalgams are regarded as chemical compounds, while the liquid amalgams may be solutions of compounds in excess of mercury, but the affinity is feeble, as the mercury is partially expelled by pressure, and completely so, in most cases, by heat. Amalgams are formed —(1) by rubbing the metal in a finely divided state with mercury, an increase of temperature facilitating the amalgamation; (2) by dipping a metal into the solution of a mercury salt; (3) by voltaic action, as when a metal is placed in contact with mercury and an acid; (4) by mixing a metal, such as gold, with an amalgam of a highly positive metal, such as sodium.

Mercury sometimes occurs in the metallic state, sometimes as an amalgam with silver, and occasionally as chloride, bromide, and iodide of mercury. The chief source of the metal is the sulphide HgS, known as cinnabar.

Lead.—This metal has a bluish-gray colour, and possesses considerable lustre; it is malleable, ductile, and tough, but has a feeble tenacity. The lustre of a freshly cut surface soon becomes dim when exposed to the air, owing to the formation of a film of suboxide of lead.

Pure lead emits a dull sound when struck, but the presence of impurities renders it more sonorous; also when the pure metal is cast in the form of a hollow sphere it becomes somewhat sonorous. Its specific gravity is 11·37, and all base metals, when alloyed with it, lower its density. Its melting point is about 330° C., and it is not well adapted for castings, since it contracts considerably on solidifying. It is so soft that it can easily be cut with a knife, and squirted into the form of tubes or rods; two clean surfaces of lead can easily be welded together by pressure in the cold, and also when in a finely divided state the metal can be pressed into a compact mass. Its specific heat between 0° and 100° C. is ·0314, and its coefficient of expansion is ·00003 for each degree between 0° and 100° C.

If lead is boiled with water containing oxygen it is partially dissolved, and the liquid affords an alkaline reaction. The metal is oxidised when exposed to moist air; it is somewhat volatile when heated in air, forming lead oxide PbO, and this oxide acts as an oxidising agent on many metals, such as copper, zinc, iron, etc. Lead and sulphur unite when heated together, forming lead sulphide PbS, which is a bluish-gray, brittle, and crystalline body.

Commercial lead is often nearly pure, but it generally contains some silver, copper, antimony, tin, and sulphur; and occasionally iron, arsenic, zinc, and manganese.

Bismuth is a hard grayish-white metal with a reddish tint and bright metallic lustre. Its specific gravity is 9·8, which may be reduced by pressure; it melts at 270° C. and volatilises at a high temperature, burning with a blue flame, forming flowers of bismuth Bi_2O_3; it expands

in the act of solidifying. When the metal is melted, and allowed to cool until its surface begins to solidify, the crust broken, and the metal poured out, fine large crystals are obtained. They oxidise in air, and frequently become covered with an iridescent film of oxide. Bismuth unites with sulphur, forming a dark gray metallic-looking sulphide Bi_2S_3.

Bismuth serves for the preparation of many pharmaceutical products and cosmetics. The chief use of the metal is in the preparation of fusible alloys, the melting points of which can be altered according to the proportions of their constituents. It occurs in nature in the metallic state, as bismuth-glance Bi_2S_3, as bismuth-ochre Bi_2O_3, and often in company with silver, lead, tin, copper, and cobalt ores.

Tin Group—Tin, Antimony, and Arsenic

§ 25. **Tin** is a white metal with a brilliant lustre; very malleable, as seen by the thinness to which tin-foil can be reduced. A bar of tin when bent produces a crackling sound, known as the "cry of tin," supposed to be due to the grinding action of its crystals over each other. Its specific gravity is 7·3, it melts at 230° C., and may be somewhat strongly heated without volatilising. When raised to a temperature near its melting point, and allowed to fall from a considerable height, the metal breaks up into the form of long grains, known as grain-tin. When tin is melted, and poured into a mould at a temperature little removed from the point at which it solidifies, the surface remains bright, if pure, but the presence of a little lead, iron, or other base metals imparts a more or less dull and frosted appearance, so that

the brilliancy of the surface is a test of purity. Tin is easily crystallised superficially by treating its surface with a mixture of dilute sulphuric and nitric acids; the ornamental appearance, known as *Moirée Metallique*, is obtained in this way. Tin is an inferior conductor of heat and electricity; it takes a high polish, and the radiation of heat from its surface is small. It forms a valuable metal for coating culinary vessels. It is little affected by air at ordinary temperatures, and is therefore used for coating iron to protect it from rust. It unites readily with sulphur on the application of heat, forming stannous sulphide SnS. Commercial tin often contains small portions of lead, iron, copper, arsenic, antimony, bismuth, tungsten, and sometimes manganese and zinc. The tin of commerce is quoted as common, refined, and grain-tin. The refined-tin is made from the best ores, and is more perfectly refined than common tin. Grain-tin is obtained from the best pigs, which are heated and dropped from a height as referred to above.

The only important ore of tin is tin-stone, which contains the dioxide SnO_2.

Antimony.—Ordinary commercial antimony is very impure, containing iron, lead, arsenic, and sulphur, and is called "regulus of antimony." Antimony is a brilliant bluish-white metal, highly crystalline, with fern-like markings on the surface, and very brittle, so that it may be easily powdered; its specific gravity is 6·72; it melts at 450° C., and volatilises at a higher temperature. It does not oxidise at ordinary temperatures, but when heated in air, antimonious oxide Sb_2O_3 is formed; and at a red heat it burns with a bluish-white flame, producing dense white fumes of Sb_2O_3.

Antimony and sulphur readily unite when heated together, forming Sb_2S_3; the same compound is also formed by heating the oxide with sulphur, thus—

$$2Sb_2O_3 + 9S = 3SO_2 + 2Sb_2S_3.$$

Antimony unites with other metals to form valuable alloys, in consequence of its hardening properties, but it impairs the malleability and ductility of the malleable metals. The effect of even small quantities of antimony on the malleable metals, such as copper, gold, iron, etc., is most injurious, making them hard and brittle.

Antimony occurs native, and in combination with other ores, but the chief ore is "stibnite" Sb_2S_3.

Arsenic.—This metal has a brilliant, dark steel-gray colour, and metallic lustre; it is crystalline, exceedingly brittle, and may be readily reduced to powder. When heated to 180° C. in a closed vessel it begins to volatilise without fusing, and crystallises as it condenses in forms similar to those of antimony. Its vapour is colourless, and possesses a peculiar garlic-like odour. The metal may be exposed to dry air without undergoing change. If heated in air it absorbs oxygen, and burns with a bluish flame, forming arsenious acid As_2O_3, which is condensed as a white powder when in contact with a cool body. The specific gravity of arsenic is 5·67.

Arsenic occurs in nature as realgar As_2S_2, orpiment As_2S_3, mispickel FeAs + FeS, nickel pyrites NiAs, and kupfer-nickel or copper-nickel $NiAs_2$.

The metal is obtained by heating nickel pyrites, mispickel, etc., in closed retorts, when the arsenic is expelled, and sublimed in condensing chambers.

Arsenic enters into the composition of some alloys,

such as shot metal, its general effect being to harden, and render the alloys brittle, and more fusible. Its compounds are used in medicine, and in glass-making.

Iron Group—Iron, Chromium, Manganese, Nickel, and Cobalt

§ 26. **Iron.**—Malleable iron is of a grayish-white colour, having a granular, crystalline, or fibrous fracture, according to the mode of treatment. When rolled or hammered hot, the iron becomes fibrous, but continued cold hammering induces a crystalline or granular structure, making it hard and brittle. The nature of the fractured surface varies also with the manner in which the iron has been broken, for specimens broken by progressively increasing stresses invariably show a fibrous structure, whilst the same specimen broken by a sudden blow may be crystalline. The presence of impurities generally tends to impart a granular or crystalline fracture, and makes the iron less malleable. When impurities, such as sulphur and arsenic, render the metal unworkable at a red heat, it is said to be hot- or red-short. On the other hand, some substances, such as phosphorus, cause iron to crack when hammered cold; it is then termed cold-short. The specific gravity of iron is about 7·8. Its fusing point is said to be about 1600° C.; but before melting it assumes a pasty form, at which point two pieces may be joined together by welding. To ensure a good weld the surfaces must be clean and the metal at a white heat. In order to dissolve any scale the smith adds a little sand, which unites with the oxide and forms a fusible silicate. The presence of any foreign bodies, such as carbon, silicon,

sulphur, phosphorus, copper, oxygen, etc., increases the difficulty of welding. Iron possesses considerable malleability, ductility, and tenacity. Its tensile strength ranges from 17 to 25 tons per square inch, but this, like all the other physical properties, is modified by the presence of impurities, which tend to make it harder, more fusible, and brittle. When iron is heated to dazzling whiteness, it burns, forming the black oxide Fe_3O_4, the iron becoming friable and brittle, and is then termed "burnt iron." Iron may be magnetised by bringing it in contact with, or near to, a magnet, but it loses its magnetism when the exciting magnet is withdrawn. Its specific heat is ·1137; its conductivity about 120, silver being taken as 1000. Its electric resistance is 5·8 times that of pure copper. When iron is exposed to moist air it readily rusts or oxidises, so that it is often coated with some substance to prevent this action, such as tinning, galvanising, and painting. Professor Barff preserves iron from rusting by exposing it at a red heat to superheated steam, which imparts to it a coating of the black oxide Fe_3O_4.

Iron may be exposed to dry air for an indefinite period without alteration, but in the presence of moisture a layer of rust Fe_2O_3 is formed. The oxidation is accelerated by the presence of carbonic acid, which is always present in the air, a carbonate of iron being formed. This rapidly absorbs a further portion of water and oxygen from the air, and in this way the rusting is slowly conveyed to the centre of the mass of iron. The layer of oxide and carbonate is electro-negative with regard to iron, so that a galvanic action is set up, causing decomposition of the water. This electrical condition still further augments the liability of iron to rust.

When iron is strongly heated in contact with air or oxygen its surface is rapidly coated with a scale of black oxide Fe_3O_4, which peels off when struck with a hammer.

Chromium is a comparatively rare metal, which only occurs in nature in combination with other elements, the chief ore being chrome ironstone FeO, Cr_2O_3. Chromium or its oxides form the colouring matter of several minerals; the green colour of the emerald, for example, is due to chromium oxide. The metal is obtained by the reduction of its oxide or chloride, or by the electrolysis of its chlorides, when chromium separates out in brittle glistening scales. It is tin-white in colour, having a specific gravity of 6·8. The fused metal is said to be as hard as corundum; it melts with more difficulty than platinum, and is only slowly oxidised when heated in air. It is used in the form of an alloy with iron and carbon, forming a hard, white, and brilliant steel, much esteemed for special purposes.

Manganese.—The pure metal, obtained by the reduction of its oxide, is a gray or reddish-white body, hard, and brittle; its specific gravity is about 8; it oxidises more readily than iron, and must therefore be excluded from air by keeping it under rock-oil, or in sealed vessels. Its chief use is in the formation of alloys with iron, steel, and copper. It is not used in the unalloyed state. Compounds of this metal are very widely distributed in nature; one of the most common is pyrolusite, or black oxide of manganese MnO_2.

Nickel.—This is a brilliant white, malleable, ductile, weldable, and very tenacious metal, with a melting point only a little below that of iron, but the presence of carbon and other impurities considerably lower its fusing point.

Its specific gravity is 8·8 ; it is magnetic like iron, but in a less degree. It does not readily oxidise in air at ordinary temperatures, but when heated the monoxide NiO is formed. It readily unites with sulphur, forming nickel sulphide NiS, which is brass-yellow in colour ; and with arsenic forming nickel arsenide NiAs.

Nickel is found in commerce in the form of dull gray cakes or cubes, and by melting these at a high temperature a compact, silver-white metal is obtained. The malleability of nickel allows of its being fashioned into various articles, which possess great lustre, hardness, and durability. These properties render it valuable for coating base metals by the process of electro-plating, especially as it is little liable to oxidation.

Commercial nickel was formerly very impure, due to the presence of carbon and other bodies, which make it hard and brittle. Dr. Fleitmann and other metallurgists have devised simple and effective means of refining and toughening nickel, which are now largely practised. Fleitmann adds to the melted metal minute quantities of magnesium in several charges, and well stirs each time a dose is added. One ounce of magnesium is sufficient for refining 60 lbs. of impure nickel. The magnesium is supposed to reduce the occluded carbonic oxide CO forming magnesia, and to cause the carbon to separate out as graphite. Nickel unites readily with most metals forming alloys, some of which are of great commercial utility. The most important of these is German silver. Nickel occurs in nature as kupfer-nickel or copper-nickel NiAs, which is a copper-red coloured mineral, with a metallic lustre. As nickel pyrites NiS, which is brass-yellow in colour. As nickel-glance, which is a variable compound

of nickel, arsenic, and sulphur. As garnierite, which is a hydrated silicate of nickel, iron, and magnesium.

Cobalt.—This metal resembles nickel in appearance and properties, and is generally associated with it in nature. Cobalt is a white metal, highly malleable, ductile, and tenacious; its specific gravity is 8·5; it is magnetic like nickel; almost unalterable in air at ordinary temperatures, but oxidises when heated, and at a high temperature burns with a red flame. It is seldom used in the metallic state, but its compounds are largely employed in pigments. It unites with arsenic to form iron-gray, fusible, and brittle compounds.

The principal ores are smaltine CoAs, cobalt glance Co_2AsS, and cobalt bloom (Co_3AsO_4, $4H_2O$).

Zinc Group—Zinc, Cadmium, and Magnesium

§ 27. **Zinc**, commonly known by the name of "spelter" when in the cast state, is a white metal, with a bluish shade, and bright metallic lustre. Ordinary zinc is hard and brittle, and when fractured exhibits a highly crystalline structure. When pure it is malleable at the ordinary temperature, while commercial cast-zinc is brittle; the latter, however, becomes malleable and ductile if heated to a temperature of 100° to 150° C., but beyond that point it again becomes brittle. Its specific gravity in the cast state is 6·9, which may be increased to 7·15 by rolling or forging; it contracts but slightly on cooling from the liquid state, and is thus well adapted for castings. The castings made at a high temperature are brittle and crystalline; but when cast near the solidifying point are more malleable. Zinc melts at 412° C., and boils

at 1040° C. At a red heat in air it rapidly oxidises, and burns with a greenish-white flame, forming zinc oxide ZnO; if raised to a bright red heat in a closed vessel it may be readily distilled. When rolled zinc is exposed to air and moisture a gray film of suboxide is formed, which preserves the metal from further oxidation. Ordinary zinc readily dissolves in dilute hydrochloric and sulphuric acids, while the pure metal is unaffected; both kinds dissolve in nitric acid and in alkalies. Zinc displaces silver, gold, platinum, bismuth, antimony, tin, mercury, and lead from their solutions. The chief impurities of the commercial metal are iron, lead, and arsenic.

Zinc and sulphur do not readily unite, but when a mixture of finely divided zinc and sulphur is projected into a red-hot crucible, some zinc sulphide ZnS is formed. It is also formed by heating zinc with cinnabar HgS.

Zinc forms compounds with phosphorus and arsenic, when these bodies are heated with it, having a metallic lustre and somewhat vitreous fracture.

The chief ores of zinc are—The oxide ZnO called zincite or red oxide of zinc, which is white when pure, but generally red from the presence of oxide of manganese. The sulphide ZnS, known as "blende" and "black jack," is the principal source of the metal, and generally black or yellowish-black in colour, but sometimes it has a reddish tint from the presence of galena; when pure it is white, and contains 67·03 per cent of zinc. The carbonate $ZnCO_3$, called calamine, is also an important source of zinc. Zinc forms with other metals a most important class of alloys, such as brass, German silver, etc. It is used in the form of sheets, worked into a variety of shapes; it protects iron from rusting, as

in galvanised-iron; it forms the electro-positive element in many batteries; and in the form of fine dust it is obtained in large quantities mixed with zinc oxide, and forms a valuable reducing agent.

Cadmium.—In the process of zinc extraction it was observed that a volatile vapour, in some cases, was distilled off with the first portions of zinc; this was found to be the metal cadmium. It possesses a tin-white colour, has a fibrous structure, and takes a high polish. It is harder than tin, malleable, ductile, and readily volatile. It has a density of 8·6; it melts at about 320° C., and boils at 860° C. Its vapour is of a dark yellow colour, with a disagreeable odour. Like tin it emits a crackling sound when bent. It is used in alloys to produce a fusible metal, which melts below 100° C.; and an amalgam of cadmium is employed as a stopping for teeth, such amalgam being soft when first prepared, but soon becomes hard.

Magnesium.—This metal possesses a brilliant white colour, but soon tarnishes when exposed to moist air, due to the formation of magnesium oxide. It is stated to possess great tensile strength, being nearly equal to that of aluminium bronze. Its specific gravity is 1·74. At a temperature of 450° C. it can be rolled and worked into a variety of forms. Screws and threads made of this metal are sharper and more exact than those made of aluminium. When ignited in a flame it burns with a dazzling white light, which is said to have been seen at sea from a distance of 28 miles. This light is used for purposes of photography. Magnesium occurs abundantly in nature in combination with other elements forming compounds, such as magnesite $MgCO_3$, dolomite $MgCa(CO_3)_2$, etc.

Aluminium

§ 28. **Aluminium.**—With the exception of oxygen and silicon, this is the most widely distributed of the elements, and contained in the largest quantity in the solid crust of the earth. It occurs in a variety of forms as oxide, but more generally in combination with other metals, such as zinc, iron, magnesium, etc., forming aluminates; as silicate in all clays, and as fluoride in cryolite ($6NaF, Al_2F_6$).

Aluminium is a white metal which takes a fine polish. It has no taste or odour. It is soft, very malleable, and ductile, with an elasticity and tenacity about equal to that of silver. Its specific gravity is 2·5, which is increased by hammering; it melts at a temperature a little above that of zinc, and is not volatile when strongly heated out of contact with air. Its conductivity for heat and electricity is said to be very high; but, according to Mr. Roby, it is very low, and diminishes the conductivity of copper considerably when alloyed with it. It does not oxidise in air or combine with sulphur; it is insoluble in cold nitric acid; sulphuric acid has no action on it; but hydrochloric acid and alkalies dissolve it readily.

Aluminium is valuable for making articles where lightness is an important feature; this, combined with its lustre, unalterability in air and sulphuretted hydrogen, non-poisonous properties, and ease of working, gives it a widespread interest. It is, however, in its alloys that its greatest value appears. In some cases it imparts strength, in others it modifies the colour, while in others it promotes soundness in castings.

Alkaline-earthy Metals

§ 29. The term "earth" was formerly used to denote those bodies which are insoluble or but slightly soluble in water, and unaltered by exposure to a high temperature. Some of these were found to have an alkaline reaction, and to easily neutralise acids; hence the term "alkaline earth." These oxides—viz. baryta, strontia, lime, and magnesia—were found to be composed of metals in combination with oxygen.

Barium is a pale yellow metal, malleable, and fusible at a red heat. It rapidly tarnishes in air, and burns brilliantly at a red heat, forming barium oxide. Its melting point, according to Frey, is above that of cast-iron. It decomposes water rapidly at the ordinary temperature. Its specific gravity is 3·75.

Strontium is similar to barium in colour; it is malleable, fusible at a red heat, quickly oxidises on exposure to air, burns brilliantly in air when heated, and violently decomposes water. Its specific gravity is 2·54.

Calcium is a yellow metal, tenacious and malleable; it melts at a red heat, oxidises in air, and burns when heated; it decomposes water rapidly. Its specific gravity is 1·58.

The alkaline-earthy metals, although their compounds are widely distributed, do not occur in nature in the metallic state, and the isolated metals have little application in the arts, on account of their easy oxidation. They may be useful in removing oxygen from other metals and their alloys.

Alkali Metals—Sodium, Potassium, Lithium, etc.

§ 30. The word "alkali" was originally used as the name of a soluble salt obtained from the ashes of sea-plants, and is now applied to a well-defined class of bodies having the following properties:—They turn red litmus blue, completely neutralise acids, are soluble in water, and their solutions exert a caustic action upon animal matter. The alkalies proper are the oxides of sodium, potassium, lithium, rubidium, and cæsium. To these is added the hypothetical metal ammonium NH_4, which is called the volatile alkali in contradistinction to potash and soda. The metals of the alkalies are soft, readily fusible, volatile bodies, easily oxidised on exposure to air; and they rapidly decompose water at ordinary temperatures.

Sodium.—This metal melts at 96° C. and volatilises, forming a dark blue vapour. It rapidly oxidises in air, and when strongly heated burns with a yellow light. It decomposes water rapidly at ordinary temperatures. It is a silver-white metal, with a specific gravity of ·97. Sodium is used for the preparation of aluminium, magnesium, boron, and silicon. As an amalgam it is used in the extraction of gold, and in the laboratory as a reducing agent. It occurs very abundantly in nature in a state of combination, in the forms of chloride, nitrate, borate, carbonate, and silicate.

Potassium.—This element is very similar to sodium in appearance and properties. It is a silver-white, lustrous metal, having a specific gravity of ·87; it is brittle at 0° C., but at 15° C. it becomes soft, malleable, and weldable; it melts at 62·5° C., forming a liquid like mercury

in appearance; at a red heat it boils, emitting a green-coloured vapour. It has a strong affinity for oxygen, and decomposes water, with evolution of great heat. It is used for similar purposes to those of sodium, and occurs abundantly in nature in analogous forms.

Lithium.—This is a widely diffused element, being found in many micas and felspars, in the ashes of plants, and in sea-water. It has the colour and lustre of silver, is soft and weldable, melts at 180° C., is volatile at a high temperature, burning with a white flame, and rapidly oxidises in contact with air at ordinary temperatures; its specific gravity is ·58, and it is, therefore, the lightest of all solid and liquid bodies.

Rubidium and Cæsium.—These rare metals so closely resemble potassium that they cannot be distinguished from that metal by many of the ordinary tests. Their presence is detected by means of spectrum analysis.

Nature of Alloys

§ 31. When two or more metals are caused permanently to unite, the resulting mixture is termed an alloy. When mercury is an essential constituent, the mixture is then termed an amalgam. The general method of effecting combination is by the agency of heat, but with certain soft metals true alloys may be formed by subjecting the constituents to considerable pressure, even at the ordinary temperature.

Alloys were doubtless first discovered by the metallurgical treatment of mixed ores, from the simultaneous reduction of which alloys would be formed; or in some cases, as in ores of gold and silver, naturally formed alloys

would be obtained by a simple melting process. The direct preparation of alloys by the simple melting together of the constituent metals has been enormously developed in modern times, and the attention which mixed metals are now receiving by chemists is far greater than in any period of history.

Comparatively few of the metals possess properties such as render them suitable to be employed alone by the manufacturer; but most of them have an important application in the form of alloys. Even among the metals which can be used independently, it is often found expedient to add portions of other metals, to improve or otherwise modify their physical properties. Thus gold is hardened, and made to resist wear and tear, as well as its cost lowered, by the addition of copper; silver is likewise hardened by alloying it with copper; and the bronze coinage is formed of an alloy of copper, zinc, and tin for similar reasons.

The purposes for which metals are alloyed are as various as the uses of the metals themselves, but, as a rule, the combination is employed to harden, render more fusible, alter the colour, or to reduce the cost of production. Thus the class of alloys known as solders, which are used for joining the several parts of a body or bodies together, are formed so as to possess melting points below that of the articles to be soldered. The well-known class of alloys termed "brass" furnishes a good illustration of the effect of alloying in producing different shades of colour. These bodies are composed of the metals copper and zinc in varying proportions, the colour depending to a great extent on the quantity of copper present. When the copper predominates the colour is yellow or reddish,

when the two metals exist in equal proportions the colour is still yellow; beyond this, when the zinc is in excess, the colour gets white, or bluish-white, resembling impure zinc. Nickel is added to brass to whiten it, forming German silver.

Again, some metals, such as copper, can only with difficulty be made to produce sound castings; and the metal is too tough to be conveniently wrought in the lathe or with the file, but when alloyed with zinc or tin, good castings can be readily obtained, and rolled, turned, or filed with considerable facility. In some cases the tensile strength of a metal is enormously increased by the addition of another metal, sometimes in very small proportions; the various bronzes may be cited as examples. The addition of a second metal is often a source of weakness, as in the case of adding antimony to lead. One might be led to consider that the alloying of two malleable metals would produce a malleable alloy, and while in many cases this undoubtedly is so, there are others in which the opposite is the fact. Thus lead added to gold in very small quantity makes the gold exceedingly brittle and weak.

The specific gravity of an alloy nearly always differs from the mean specific gravities of the constituents, sometimes being greater and sometimes less. When the density is increased it shows that contraction has occurred, and chemical combination has probably taken place between the components. This is the case with bronze rich in copper, while with similar alloys rich in tin expansion occurs, the specific gravity being less than the mean of the two metals. One of the greatest difficulties connected with the subject of alloying is the tendency of

the constituents to separate on cooling according to their specific gravities. As a rule, it is more difficult to alloy three or four metals than two metals, especially when the components differ widely in fusibility, unless the combination forms a true chemical compound. The mixture is promoted by constant agitation when the body is in the liquid condition, and by pouring the metal into the mould at the lowest possible temperature consistent with the proper degree of liquidity.

Most metals are capable, to some extent, of existing in a state of chemical combination with each other, but, as a general rule, they are united by feeble affinities, for it is necessary, in order to produce energetic union, that the constituents should exhibit great dissimilarity in properties. It is probable that the metals do unite in definite proportions, but it is difficult to obtain these compounds in a separate condition, since they dissolve in all proportions in the melted metals, and do not generally differ so widely in their melting points from the metals they may be mixed with, as to be separated by crystallisation in a definite condition. For these reasons it has been questioned whether alloys are true chemical compounds. Definite compounds do, however, exist in definite proportions by weight in the native as well as the artificial state. Such is the case with mercury and silver, which are found crystallised together in the proportion of one atom of silver to two or three atoms of mercury. A good illustration of chemical combination between two metals is seen in the alloy of copper and tin, which may be represented by the formula $SnCu_3$, containing 38·4 parts of tin and 61·6 parts of copper. It is distinguished by its peculiar colour, its homogeneity after repeated fusions, its brittle-

ness, and by having a greater density than any other alloy of these metals.

As a general rule, it may be stated that all metals which unite with oxygen to form only bases, have a strong tendency to unite with metals, some of whose oxides possess an acid character; and those metals which are allied in regard to basicity or acidity, have little affinity for each other. Thus sodium and potassium, although miscible in various proportions, exhibit little or no tendency to unite in definite quantities; and the same is true of antimony and tin. On the other hand, copper and tin form very stable alloys. In some instances, as in the case of the metals lead and zinc, only very unequal portions can be made to unite, the main bulk of the metals separating on cooling; the lead retaining 1·6 per cent of zinc, and the zinc retaining 1·2 per cent of lead. In all cases of mixed metals there is not that total and complete alteration in physical characters which is the distinctive feature of chemical action between a metal and a non-metal. Alloys still possess the metallic character, but there is frequently a considerable evolution of heat evinced; the melting points, as in fusible metal, are considerably lowered; the mean density is increased, and the colour and other physical properties are considerably modified.

Most often, however, as already indicated, alloys seem to be mixtures of definite compounds with an excess of one or other metal, and the separation of their components from each other is generally easily effected by simple means. Thus an alloy of lead and copper may be largely separated by exposing the mixture to a temperature a little above that of the fusing point of lead, when the latter metal liquates out, leaving behind a porous mass of

copper, containing a little lead. Also in remelting brass a considerable quantity of zinc is lost by volatilisation. When silver is amalgamated with mercury the amalgam is dissolved in an excess of mercury, which excess may be removed by simple pressure; and the remaining portion of mercury is completely separated by the agency of heat.

Many metals combine together when melted, and only remain in union within certain ranges of temperature, as shown by the wide differences between their melting and solidifying points.

NATURE AND OBJECT OF METAL-COLOURING OR BRONZING

§ 32. The object of bronzing metals is partly to beautify the exterior by imparting to it a coating or surface film of colour, which the common metals do not naturally possess after a short exposure to atmospheric influence; and partly to protect the surface from further discoloration, produced by the combined action of air, moisture, and various gases, with which the air often becomes adulterated, especially in large towns and places where coal-gas is largely burnt.

During the process of natural atmospheric metal-colouring, which may extend over years and even ages, the change is very gradual and by no means uniform in its extent, for one part of a body is usually affected more than another, or one portion may be corroded while another portion remains unaltered, doubtless depending on the irregular condition of its surface; for, as the author has repeatedly experienced in practice, it is absolutely essential that every part of the exterior should be in exactly the same physical condition for a uniform tint to prevail all over. Metals, with few exceptions, become altered on their surfaces by continued exposure to the atmosphere, and it is to such alterable metals that the process of bronzing is chiefly ap-

plied. The metals which combine directly with oxygen gas are termed "base" metals, and the product of their oxidation is an oxide. This is the kind of change which most frequently occurs on exposure to air, producing the well-known substance commonly called rust, and for this reason it is generally necessary to coat them with some protecting film in order to protect them from the action of the atmosphere. Some of the base metals are more easily corroded than others, and those metals least affected in air are often employed to form a protective covering on those metals which are most easily affected. For this reason iron is coated with tin or zinc, or electro-plated with nickel. Brass and its various other alloys are also coated with silver, and sometimes with gold for the same reason.

The element copper, both in the pure and in the alloyed state, is the metal *par excellence* which lends itself most effectually to the production of beautiful bronze tints. This is in a great part due to its red colour, which may be altered into a great variety of tones and half-tones by various solutions, chiefly solutions in which its own salts are present as essential ingredients. It is well known that articles of copper and its alloys, after a long exposure to the action of the air, acquire a beautiful brown or green colour, which considerably contributes to their handsome appearance. This colour is known as *Ærugo nobilis* (noble rust) or "patina." The green colour is due to the formation of a basic carbonate of copper, falsely termed verdigris, and is often associated with brown and blackish tints, especially on very old bronze medals and statues. No artificial colouring can compare in beauty and durability with the natural patina.

In order to obtain a coating similar to genuine patina,

it is recommended to pursue, as nearly as possible, the same course by which the latter is naturally formed. By the action of air and moisture which contain minute quantities of salts in solution, the copper is attacked, and in course of time the basic carbonate of copper is formed by the agency of carbonic acid. This is often associated with copper sulphide, which accounts for the dark tones alluded to above.

It will thus be seen that the natural coloration of bronze is a chemical process produced by gradual chemical changes, resulting in a complete alteration of the surface, and if a similar effect is to be produced on the surface of metals by artificial means, a chemical process must be resorted to.

But metals are often coloured by mechanical means, such as painting, lacquering, and varnishing. This is not bronzing in the original sense of the word; and however highly a metal may be coloured by such means, it always lacks that peculiarly beautiful effect generated by chemical agency, and has a more or less common look in proportion to the effacement of the metallic character.

Chemical action is often promoted by the influence of electricity, and such a change may be termed "electro-chemical." Very beautiful results in the coloration of metals may be achieved by this agency, either by a chemical change of the surface, or by the electro-deposition of one metal on another. Bronzing or metal-colouring may therefore be considered under the following heads, viz.—

§ 33. I. Chemical Metal-colouring, produced by a corrosion of the surface by chemical agents. In this method the surface film of metal is changed into a chemical compound, having a colour peculiar to itself

under definite conditions, but which may be modified by various circumstances, such as the nature and colour of the metal which forms the base, the temperature at which the change occurs, and the thickness of the layer of the compound itself. In fact, the same chemical compound may exist in different modifications of colour, varying, as in the case of cuprous oxide, from bright red to dark brown.

But the change occurring on the surface of metals by chemical bronzing is often the result of complicated chemical changes, which produce more than one compound, each of which exercises an influence on the colour according to the relative amount of each constituent. Thus in oxidising copper, for example, both its oxides may be formed, the cupric oxide which is black and cuprous oxide which is red, each colour modifying the other in tone.

§ 34. II. Electro-chemical Metal-colouring.—This may be brought about by coating a metal, wholly or in part, with a very thin film of another metal, the shade of colour of which may be modified by the temperature and strength of the electric current employed. Nobili's figures or electro-chromes are illustrations of electrical metal-colouring. All methods of deposition, whether by simple immersion, or by immersion and contact with another metal, will be considered under this head.

§ 35. III. Mechanical Metal-colouring, such as coating a metal by the superposition of paint, lacquer, varnish, or bronze powders, by means of varnish or other adhesive material on its surface, but which coating does not enter into chemical combination with the metal or in any way alter its properties. There are other means, of a purely mechanical character, by which the colour of a metal

may be altered. If, for example, we look along the surface of a plate of gold at a great angle it appears very brilliant, but almost white in colour, but if we view it at a small angle the natural yellow colour appears. It may be still further developed and enriched by repeated reflections at a small angle of incidence. It is for this reason that chased gold and "granulated" gold appear of a far richer colour than burnished gold; and by so shaping the grooves or lines of chasing upon any piece of coloured metal that repeated reflections at small angles of incidence occur in them very beautiful tones of colour may be produced.

Some metals which lack distinctive colour under ordinary conditions may be thus made to develop it. Yet the colour so produced not only changes in purity and brightness as it becomes enriched, but its hue is also modified. Thus copper may be made to yield ultimately a nearly pure or monochromatic light by repeated reflections. The colour is more decided, it is purer; but there is less light.[1] In fact, anything which alters the evenness, or breaks the continuity of the surface of a metal will not only modify its colour, but impart different shades of colour in different parts. This method of treatment is chiefly applicable to the noble metals, since the common metals soon change when exposed to atmospheric influences, and the effect is gradually destroyed.

§ 36. Up to about seventy years ago the only artificial bronze employed for copper and its alloys seems to have been the various shades of antique green, to which the name patina was exclusively applied. But since that time the meaning of this word has been expanded so as to

[1] *Colour*, by A. M. Church, p. 160. Cassell and Co.

apply to all colours produced on metals by way of bronzing.

About the year 1828 the now celebrated Florentine bronze was introduced by a Frenchman named Lafleur, and soon became very popular. The colour has remained in favour to the present day in consequence of the variety of agreeable brown shades which can be produced on copper and its alloys by means of iron oxide and other agents, causing the formation of a mixture of cuprous and cupric oxides on the surface. Following this many new bronzes were introduced in this country and soon acquired considerable notoriety. It is a cause of great regret that this art has been allowed to deteriorate of late years in England, and that such a valuable industry has passed into the hands of foreigners. In 1833 the Germans began to apply metal-colouring to articles made of cast zinc, which was soon taken up in France, and the refined taste of the French soon enabled them to adapt the principles of metal-colouring, both chemical and mechanical, to all metals, and to become the acknowledged authorities on the subject. They combined the two methods so as to produce a variety of colours on the same article, such as the original greens with the Florentine browns. Also they made the groundwork black or dark coloured, with yellows, greens, and browns, on the embossed parts, the latter being bronzed by means of varnish and bronze powders. During the last fifty years great strides have been made both by the French and Germans, and although the productions of some of the early workers have never been surpassed for beauty of tone and perfection of finish, the art has now a much wider and more extensive application. The number of solutions available for

bronzing is largely increased, with a consequently extended variety and shades of colour. Moreover, the number of alloys has been enormously extended of late years, so that the art bronzer has a much greater variety of materials at command on which to exercise his skill.

Mention has already been made of the admirable skill displayed by the Japanese in combining different coloured alloys, as well as in the production of bronzing effects on the surface by means of different pickling solutions. This nation and the French and Germans are pre-eminently the masters of the world in the art of metal-colouring. Their styles are different, each has its own particular modes of treatment, and in consequence of this it is impossible to say which occupies the first position. Undoubtedly the French and Germans are without equals in Europe, and with regard to chemical metal-colouring they probably surpass the Japanese, especially as their ordinary chemical knowledge enormously exceeds that of the Japanese. The Viennese among European nations have attained great excellence in the colouring of metals, and come very near to the French in artistic merit and scientific knowledge of the subject.

§ 37. Metal-colouring is essentially associated with art, and no workman can beautify a metal without he possesses some artistic taste. It has, unfortunately for us, become the idea among many manufacturers that bronzing is a very simple mechanical operation and can be left to an ordinary dipper to accomplish, who may not have learned the art, and who may not have the remotest idea of the nature and harmony of colour. It is quite true that the cheap work, coloured in monochrome, does not require much knowledge and skill, and cheap labour can be

obtained to do it. But there is as much difference between true artistic bronzing and mere dipping, as there is between whitewashing a wall and painting a meritorious picture. Other nations have grasped this difference and take care to provide skilled labour, and until we do the same we must continue to send our best work to a foreign country to be executed.

We do not sufficiently realise how exceedingly beautiful a common metal can be made to appear with little expense as regards materials, if only tastefully and suitably coloured. An effect can be produced by bronzing on a metal peculiarly its own, and which cannot be produced on any other material so as to give the same satisfaction, or to have anything near the same appearance. The suitable colouring of a metal then is not a matter of subordinate importance but of the highest significance if we are to get from it the utmost pleasure and profit it is capable of yielding

The superiority of French workmanship is doubtless due to art and scientific training, the combination of theory and practice, so that while a change is taking place, or a particular solution is selected, the operative has an idea of the effect the desired colour will have on the final result, and a knowledge of the chemical change requisite to produce that result. Every year adds to the sum of human knowledge with regard to chemical change, and therefore to the possibilities of an art which is so essentially a chemical one.

No mere recipe will be sufficient to enable a person to produce a given colour, as each metal not only has an individuality of its own, but is modified, sometimes to an enormous extent, by even small traces of an impurity, and an alloy of two or more metals may vary in its action with a given solution according to the proportion of the constituents present.

I have seen varieties of brass, differing but slightly in composition, behave quite differently in the same solution, and the same metal will often take a different shade of colour in the cast state to that in the rolled or stamped state.

The art bronzer should therefore, in addition to his knowledge of the principles of colouring, have a fair knowledge of chemical and metallurgical principles, especially of alloys. Some solutions after serving their purpose as bronzing reagents may contain valuable ingredients which will pay for their recovery, and, with a knowledge of chemistry on the part of the operator, may be profitably extracted. Some solutions depend for their success on the purity of the chemicals employed as well as on the composition of the metal required to be bronzed, and it will be a great assistance if the bronzer is capable of testing such solutions and metals as to their degree of purity.

The author, in some experiments on bronzing brass articles of different makers in a certain solution, found that the alloy from one firm gave a very beautiful colour, varying from light gray to black, according to the length of the time of immersion, while a similar kind of metal from another source acted quite differently. Great importance therefore is attached to a thorough knowledge of the nature and composition of the materials operated upon on the part of the workman, if the best results, which a given combination is capable of yielding, are to be secured.

Again, many failures result from a disregard of time and temperature during the bronzing operation. Some liquids work best at the ordinary temperature for the production of a given shade of colour, but in the majority of cases solutions are best worked hot. Some require to be used at a boiling temperature, while in

others better results may be obtained at a temperature of 60° to 70° C. Most metals act differently in the cast state to what they do when stamped or rolled, and here a metallurgical knowledge is of great value.

Lastly, a knowledge of the principles and practice of electro-metallurgy is of the greatest importance to the art bronzer. In fact, very limited results can be achieved without recourse to this valuable art. As already remarked, a given bronzing liquid affects different metals in different ways as regards colour, and by depositing copper, brass, nickel, silver, etc., on different parts of an object a great variety of colours may be produced when such a complex metallic surface is subjected to the influence of a bronzing solution. The groundwork may thus be made to assume a dark or light tone, and each portion may be induced to accept that particular tone which is in most perfect harmony with its prominence in the design.

It should also be borne in mind that a metallic article is not like canvas or paper, which has to be completely covered with paint of all colours from the brightest scarlet to the dullest gray, but a material which must always assert its peculiar metallic character, so that there is never any doubt as to its real nature. It is true, that a bronzed metallic article is not coloured so that one may say whether it is made of copper or brass or spelter, but the colours must always allow the beholder to say without hesitation that the base is a metal and not wood or any other material.

The above remarks are not completely applicable to the precious metals. Gold, for example, apart from its monetary value, is an exceedingly beautiful metal as regards colour and lustre, and is not altered by exposure to the atmosphere, nor by sulphur, so that bronzing of

gold is entirely opposed to the nature of the metal, and therefore scarcely a legitimate process. There should never be any doubt about a gold article whether it is gold, and to make it look like a base metal would be quite opposed to artistic taste. Slight differences of tone may be obtained by alloying gold with other metals, and the intensity of the reflection enables jewellers to use these coloured varieties with the best effects.

Another argument why gold should not be debased has already been mentioned—viz. that gold has above every other metal the property of harmonising with, and setting off, all ordinary colours, whether metals or pigments. Two instances may be noted—the gilt frame of a picture and the gold threads in embroidery. Gold, in fact, is removed from the series of ordinary paints and dyes by its great lustre, and so combines into agreeable assortments with all colours, even with those with which yellow and orange pigments do not associate well. In a picture frame this peculiarity of intense reflection prevents its yellow colour from interfering with the similar hues of the picture, while its colour, being luminous and "near," gives the idea of some degree of distance to the picture itself.[1] Silver differs from gold in the fact that it is tarnished by sulphur and sulphur compounds, although it is not affected by pure air. Hence, silver may very fittingly be bronzed, or, as it is erroneously termed, "oxidised." In many cases the exceeding whiteness of pure silver forms too violent a contrast to other metals, and the general effect is greatly improved by toning down this great lustre by one of the so-called oxidising processes. Yet the silver should still convey

[1] *Colour*, by A. H. Church, p. 163.

the impression that it is silver and not lead or some other base metal.

§ 38. It is of the utmost importance then that a bronzer should have clear conceptions of the principles laid down in the preceding pages, so as to treat each metal or combination of metals in a manner for which it is best adapted. Some persons have the impression that the colour of a liquid imparts its own colour to the metal, like fabrics receive their colour in dyeing. That this is not so will soon be evident after a few experiments on colouring metals. The colour of the solution employed is no criterion whatever as to the colour the metal immersed in it will receive.

It should be borne in mind that the surface colour the metal will assume will depend on the power of the solution to effect a chemical change, and produce a coloured compound of the metal with other elements, such as oxygen, sulphur, chlorine, etc. The colour will depend on the condition, uniformity, and cleanness of the surface, and not entirely upon the cleanness of the solution in which it is immersed. It is not a matter of indifference, as already mentioned, whether the article to be coloured is made of cast or rolled metal, or whether it is an electro deposit, as in the case of copper, for example, for each physical condition has a great influence in modifying the colour. In most cases, the smoother and more regular the continuity of the surface, the more uniform will the colour be.

The natural physical condition of a metal appears, in most cases, to be crystalline or semi-crystalline, but by mechanical treatment this structure may be so altered as to confer on the metal new properties. It may become granular, fibrous, or vitreous in structure, and when this

alteration extends to the fundamental parts or molecules, the metal may be so changed as to act like an entirely different body. Cast zinc, silver, gold, and nickel have their crystalline condition destroyed by rolling, while tin, lead, and brass may be less altered. On the other hand, many chemical agents, as well as mechanical forces, have power of changing fibrous or granular structure back to the crystalline condition.

All these conditions therefore influence the power of a given solution to bring about a certain change in the chemical colouring of metals. It is of importance to consider the size of an article as well as the degree of dilution of the bronzing agent with reference to the time required to effect a chemical change. Two things may be considered—a short time under the influence of a strong solution, or a longer time under the influence of a weak solution. The first condition is preferable, if the desired colour can be obtained in a uniform layer, but the second condition is found to be generally most effective. The temperature at which the bronzing is effected has also to be considered. If the operation can be performed in the cold, even at the sacrifice of longer time, it is far more convenient and desirable, especially with large articles. There is always a difficulty in obtaining vessels large enough to hold articles of great size when the solutions have to be boiled or strongly heated.

Moreover, many bronzing solutions have a strong corrosive influence on the materials of which the vessels are usually made, and this destructive power increases with a rise in temperature. Copper vessels are generally best for hot solutions. A metallic vessel, such as iron, will decompose some solutions, and enamelled iron

pots soon wear away when in constant or frequent use. If, therefore, the bronzing can be done at the ordinary temperature, earthenware vessels may be employed, which are the best whenever their use is admissible.

§ 39. It is advisable to use simple salts for solutions, if they are capable of producing the desired effect, as a mixture of two or more salts, although often necessary, will not long remain uniform, and after several articles have been bronzed will begin to produce a lighter tone of colour. Of course this is not always a disadvantage, as in some cases the lighter colour may be preferable to a darker one, and consequently some solutions are more valuable after they have been worked some time. In all cases, whether a solution contains a single salt or a mixture of several salts, it will become exhausted after a time and require renewing by the addition of fresh salts.

It is generally better to dissolve a salt before adding it to an old solution than to add it in the solid state, or considerable time may be lost while waiting for it to completely dissolve. It often happens that a solid salt added to an old solution will fall to the bottom and become covered with the insoluble mud, which will prevent its being dissolved unless the solution is constantly agitated and heated; sometimes it is necessary to raise the whole bulk of solution to the boiling point before complete solution occurs, while the salt itself may be fairly soluble in a comparatively small quantity of clean boiling water.

As previously stated, the number of colours a metal is of itself capable of assuming will largely depend on the colour of its various compounds with oxygen, sulphur, etc., and it will greatly assist the operator in his work if he knows the number and nature of the different

coloured compounds which a given metal forms, and the ordinary chemical means of producing them. Take iron, for example; we know that there is a black and a red oxide of iron, each being produced by oxidation—one at a high temperature and the other at a low temperature. We also know that the red oxide is modified in colour tone, from a deep red through various shades of reddish-brown to brown, and finally to a dark brownish-black, by varying degrees of heat, and by a partial deoxidation, if another body is present which has a strong affinity for oxygen.

Copper also forms two different oxides—viz. red and black oxides, according to the degree of oxidation, and this power of being coloured by oxidation is continued in a modified degree in many of its alloys. On the other hand, the metal zinc has few available coloured compounds, and a direct bronzing of zinc is therefore difficult by any chemical process, and it becomes advisable to associate it with a metal, such as copper, which possesses coloured compounds, either by alloying or by electro-deposition, in order to impart to it a bronze tone.

But other conditions are necessary for bronzing besides the production of coloured compounds on the surface. The colours should be beautiful and artistic, firm, uniform, and consistent with the metallic character. Many beautiful colours are obtained in bronzing solutions which, if the deposits were firmly adherent to the metal, would be very valuable, but unfortunately they are swilled off by the wash-water to the great disappointment of the experimenter. Another annoyance which one often encounters is the non-uniform character of the coloured surface. But this, in many cases, can be remedied by the scratch-brush and polishing bob, and by another immersion.

PART II

PRELIMINARY TREATMENT OF METALS FOR COLOURING

A. CLEANING

§ 40. In the first place, it is absolutely essential that any article or portion of an article to be bronzed by chemical means should be perfectly clean, as any dirt, grease, or oxide stains, although invisible to the naked eye before the body is placed in the pickling solution, will be at once revealed after the process, showing up as ugly stains. After cleaning, the article should not be touched with the hands, or exposed to air any longer than necessary before being suspended in the bronzing solution, or the surface will be altered and the subsequent bronzing defective.

The article should be cleansed from dirt by washing with water and brushing with fine sand, pumice, whiting, etc., so as to remove all matter simply adhering to the surface. Grease and fatty matter as well as lacquer on old work may be best removed by boiling in a hot solution of caustic potash or soda, contained in a cast-iron pot. The articles should be suspended by means of wire previous to immersion to avoid handling as much as

possible. After boiling for some time they should be removed, and if not perfectly clean it may be necessary to scour with fine sand, swill in water, and again suspend in the solution.

Small articles may be freed from grease by dipping in benzine or paraffin. The best plan is to have three vessels containing the cleansing liquid. The first is used for dipping the articles so as to remove the greater portion of the grease by frequent dipping in and taking out to examine. The second dip is more pure and is used for removing the remainder of the dirt. The third or clean dip is used for removing the last traces that may not have been completely removed in the second bath. The article after removal from the third bath is left in the air to dry. The first and second dipping liquid may very conveniently be paraffin, and the third benzine. It should be observed that these liquids are very inflammable, and therefore must be removed from the vicinity of a naked light, especially in the case of benzine.

Large and bulky articles, such as copper, brass, iron, and bronze goods, are best cleansed from grease in boiling potash or soda solution. One lb. of potash to 1 gallon of water is a convenient quantity to make a strong solution. It should be borne in mind that in boiling this solution the water only evaporates, leaving the remainder in a more concentrated state, so that the solution should be frequently made up with water, thus keeping the solution at a constant amount.

Zinc and tin articles may also be cleansed in potash solution, but care is required, as these metals are somewhat soluble in this liquid, and the fine lines of the pattern are liable to be removed. The best plan to adopt

in the case of zinc is to allow it to remain only a short time in the solution, then to take it out and scrub it with a brush which has been dipped in fine wet sand. Care must be taken to thoroughly swill the cleaned articles in two or three lots of wash-water so as to remove every trace of potash, especially with zinc and tin articles. Moreover, the articles must be kept immersed in perfectly clean water until they are ready for the acid dip and bronzing bath, as they will tarnish if exposed to the air. Caustic potash or soda solution lasts a long time, and when it is partially exhausted, may be renewed by adding fresh portions of the solid salt.

Another liquid in constant use for cleansing purposes is a solution of potassium cyanide. Potash and soda solution themselves act as bronzing liquids in some cases, and most metals are coloured more or less when immersed in them, especially when the solutions have been in use for some time. This is not always a defect, but occasionally it is important that the articles should leave the dipping liquid perfectly uncoloured, and then a solution of potassium cyanide is valuable. About 1 lb. of good potassium cyanide dissolved in 1 gallon of water makes a solution of convenient strength.

Besides dirt and grease which may be removed by the methods just enumerated, articles are often coated with a film of some firmly adherent chemical compound which can only be removed by means of an acid, and therefore is not soluble in water or the liquids already described.

§ 41. (1) **Copper and its Alloys.** — Copper, brass, bronze, etc., become oxidised in ordinary moist air, and, in consequence of the simultaneous presence of carbonic acid, become gradually converted into carbonates. In fact, the

brownish-black to bluish-green deposit, often seen on copper, brass, and bronze goods, is a mixture of oxide and carbonate of copper, mixed with oxygen compounds of zinc or tin respectively when the copper is present as an alloy of these metals. Sulphur compounds are often formed on the surface, when the above metals are exposed for some time to the atmosphere of large towns or rooms where coal-gas is burned.

These films may be removed by immersion in suitable acid dips. For this purpose a series of liquids is used: pickle or spent aquafortis is very generally employed for a preliminary dip. The articles are allowed to remain in it until the scale of oxide has disappeared, leaving, after rinsing, a uniform metallic lustre. Dipping in old aquafortis is recommended for two reasons: it economises the cost of new acid, and, as its action is slow, it prevents the too rapid corrosion of the cleansed copper during the time of the solution of the protoxide. A dipping liquid consisting of a mixture of 64 parts commercial sulphuric acid, 32 parts of aquafortis, 1 part hydrochloric acid, and 64 parts water is also used.

§ 42. Copper, brass, bronze, German silver, etc., are often cleaned by heating them to dull redness, and then plunging into dilute sulphuric acid. (Those having solder upon them are not heated thus; neither are articles of cast-bronze, because they would be liable to crack.) They are then soaked in old aquafortis, until, after rinsing, they look uniformly metallic; they may then be dipped in strong aquafortis for a few seconds and swilled. The straw-coloured aquafortis acts the best; the white variety acts too feebly, and the red too strongly. It is best to use the dips cold, and to have a considerable bulk

of liquid to prevent them becoming too hot by the immersion of the heated metal.

In diluting strong sulphuric acid with water a considerable amount of heat is generated by the chemical action which takes place between them, and if the mixing is made too rapidly the vessel which contains the mixture is liable to be cracked and the liquid to be projected on to the operator. The acid should always be poured into the water and not *vice versa*.

To dip gilding metal bright. Immerse it in weak aquafortis until there is a black scale formed, then dip it in strong pickle for a few minutes (*N.B.*—Strong pickle is partially exhausted aquafortis; weak pickle is the same diluted with the washings), then dip it quickly into aquafortis, then into several wash-waters in succession.

There are various mixtures which may be employed for imparting a bright lustre to brass, German silver, etc., by dipping; the following is one of them :—1 measure of nearly exhausted aquafortis, 2 of water, and 6 of hydrochloric acid; the articles should be immersed in it for a few minutes, or until, after washing off the black mud which entirely covers them, they look bright; they are then cleaned and dipped again. It is convenient for removing the sand, etc., which adheres to castings. Large articles may remain in this bath for twenty to thirty minutes.

§ 43. **Dipping in Aquafortis, Common Salt, and Soot.**—Brass and similar articles, after cleaning in pickle, are rinsed in water, well shaken and drained, then dipped in a bath consisting of 100 parts nitric acid, 1 part of common salt, and 1 part of calcined soot. This mixture attacks the metal with great energy, and therefore it should only remain in it a few seconds. The volume of

acid should be twenty times that of the articles immersed in it to prevent undue heating and too rapid weakening of the acid. When removed, the articles should be quickly rinsed in water to prevent the production of nitrous fumes. They then present a fine lustre varying from red to golden-yellow and greenish-yellow, according to the composition of the alloy.

If the metal is not swilled in water after removing from the acid, there rises on its surface a green froth, and nitrous vapours are given off which indicate the decomposition of the acid with which the metal is covered. When the vapours have disappeared the metal remains dull black, even after swilling. This last mode of operating, called blacking by aquafortis, is used by some colourers to give a dull dark colour to brass and bronze work. Aquafortis is spent when its action on copper alloys is too slow, and when the objects removed from the bath are covered with a bluish-white film. Such acid is termed "pickle," and is used for the preliminary cleaning, or for forming what is termed a whitening bath. Very good aquafortis may appear too weak and cleanse imperfectly by dipping when the temperature is too high, or when it is too low, as in the case of frosty weather.

§ 44. **Whitening Bath.**—This consists of old aquafortis, sulphuric acid, common salt, and soot. Pour into a stoneware vessel a certain quantity of old aquafortis, and add twice the volume of commercial sulphuric acid. Allow the mixture to stand till the next day. The copper nitrate of the old aquafortis is converted into copper sulphate, which crystallises against the sides of the vessel. Decant the clear liquid into another vessel and add 2 to 3 per cent of common salt, and an equal quantity of calcined

soot. This mixture is less active than the acids used for a bright lustre. The bath may be strengthened when necessary by the addition of aquafortis and sulphuric acid.

§ 45. Another dipping liquid may be made with equal parts of aquafortis and sulphuric acid mixed with forty times their bulk of water and allowed to cool, then adding a quantity of common salt equal to about one-fifth that of the strong acid present. Or the following may be used:—

1½ lbs. nitric acid,
2 lbs. sulphuric acid,
10 grains common salt.

To the above ingredients add a mixture of the following if a dead surface is desired :—

1 lb. nitric acid,
½ lb. strong sulphuric acid,
5 grains common salt,
20 grains zinc sulphate.

The longer the articles remain in this dip the deader will be the surface. They are then thoroughly swilled and dried as quickly as possible. Or previous to swilling with water they may be momentarily dipped in the bright dipping liquid.

Mr. Aitkin says that "dead dipping" was discovered in the following way:—In the year 1832 a dipper in the employ of Mr. David Malins of Birmingham left throughout the night a quantity of articles in the pickle, and when he attempted to produce the bright appearance in the bright dip they presented a dull frosted yellow surface. Charmed with the effect, certain portions were burnished and the whole lacquered. Acting on the accidental hint,

dead dipping was originated, and has now become the recognised mode of finish for brass work generally.

Another liquid for dead dipping made may be made of—

1 volume of a concentrated solution of potassium bichromate,
2 volumes of concentrated hydrochloric acid.

The articles should be left in this solution for some hours, then well swilled in several wash-waters. If, however, they are left exposed to the air for some time without lacquering or further treatment they become coated with a film of oxide. Dead dipped articles, while waiting to be bronzed or lacquered, may be kept from oxidising by immersing in clean water, to which half its volume of alcohol has been added.

In the case of copper alloys, such as brass, the surface colour will depend not only on the original composition of the alloy, but also on the length of time it has been exposed to the action of the acid. The zinc is oxidised more rapidly than the copper, so that the effect of dipping in aquafortis or other oxidising liquid is to increase the relative quantity of copper on the surface, and to give to the alloy a richer appearance and a deeper colour. When it is desired to clean very small articles and not to appreciably alter the composition, they may be dipped in a solution of 5 parts potassium cyanide dissolved in 95 parts of water.

If the coloured brass articles show a granular appearance on the surface after dipping, they should be immersed for twelve hours in a mixture of 1 volume of nitric acid, 1 volume of sulphuric acid, and 8 volumes of water. The grayish-black deposit is washed off with water, leaving

an agreeable moiré appearance. The articles are next immersed in one of the bright dips above described, then passed through a weak solution of caustic soda, or milk of lime, well washed in water, and dried out in sawdust.

If an article remains too long in the bright dip, after being made dull in the dead dip, the dead lustre disappears. If the bath for giving a bright lustre is not available, the objects, after rinsing, may be rapidly passed through the dead dip to remove the dulness of the lustre caused by too long immersion. After long use the compound acids used for bright dipping will give a dead appearance to brasswork. For large embossed work a hot bath for dead lustre is used, composed of—old aquafortis, 4 to 5 parts; sulphuric acid, 1 part; zinc sulphate, 8 to 10 per cent. More zinc sulphate is added when required for increasing the dulness of the lustre. The lustre, however, after rinsing the article, and passing it through the same bath for one or two seconds, and well swilling, becomes clearer.

For the production of a granular appearance on brass, etc., a mixture of one part of a saturated solution of potassium bichromate in water, and two parts of concentrated hydrochloric acid, may be employed. The metal is left for some hours until the desired granular effect is produced. It is then removed and well swilled with water. The operation may be considerably hastened by the aid of an electric current, attaching the metal article to the positive pole of the battery and using a brass plate as the cathode. The liquid for this method may be a very dilute solution of sulphuric and nitric acids, or of potassium bichromate and hydrochloric acid.

§ 46. When a dipping liquid becomes nearly exhausted, or when an article is immersed for too long a time, the

surface assumes a dark blackish-gray appearance, or becomes patchy in parts, as the metal is not acted upon.

The metal may be restored to its right colour by dipping it in a solution of zinc chloride, taking out, heating till it is dry, and washing in water. This method will also serve for the bright dipping of brass in case it has only a very thin film of oxide to be removed; the metal must in this case be dipped, boiled, and well washed.

Old aquafortis may be revived, to a certain extent, by the addition of sulphuric acid and common salt; the sulphuric acid decomposes the copper nitrate in it, and also the common salt, and sets free nitric and hydrochloric acids. Crystals of copper sulphate also form at the bottom of the liquid. All the nitric acid may be utilised in this way.

For dipping small articles they may be either strung on wires of the same or similar metal, or put into a perforated stoneware basket and then dipped. It is best for the suspending wires to be of the same material as the articles, because they are then less liable to cause a stain. It is less economical, but sometimes necessary to use baskets of brass or copper wire cloth. Those who have frequently to cleanse very small articles will find it advantageous to employ a basket of perforated platinum foil, which, though expensive in the first cost, will be found the most economical in the end, as it is not acted on by single acids.

§ 47. (2) **Zinc.**—When clean zinc is exposed to the air, even at ordinary temperatures, a thin gray film of suboxide of zinc soon forms on the surface, which protects the metal beneath from further oxidation. If the metal

has been exposed for a long time to the atmosphere of a large town, or to the action of impure water, the film becomes more firmly adherent to the metal, and is composed of other bodies than the sub-oxide. When the film is composed only of oxide and is very thin it is very readily dissolved in a dilute solution of sulphuric acid (15 to 20 parts water to 1 part of acid).

For the thicker and more complicated film, mentioned above, a cold mixture of equal parts of sulphuric and nitric acids is best. As great heat is produced by this mixture the whole must be cooled before using. The zinc article to be cleaned should be suspended for a second or two in this dip by means of a wooden support, then swilled several times with water so as to remove every trace of acid. It is a good plan to let water finally run on the article straight from the tap to ensure a perfect cleansing. The zinc should then be bright and clean.

Acid dips for zinc become gradually weaker with use, since the oxide of zinc is dissolved, and combines with the acid to form zinc sulphate, or a mixture of zinc sulphate and nitrate according to the composition of the solution. Such a liquid will still possess cleansing properties, but will act much more slowly, and the zinc immersed in it, instead of coming out bright, will be dull, or crystalline. The dip may in such a case be renewed by adding a little concentrated sulphuric acid. If the zinc article has been coppered and it is required to clean it, it must be dipped in aquafortis till it becomes black, then dipped in one of the former solutions.

If it is desired to produce a dull appearance on the surface of the zinc, it should be first dipped in dilute sulphuric acid or a mixture of sulphuric and nitric acids

which has become nearly exhausted by use with zinc articles, then put into a bath consisting of zinc nitrate dissolved in very dilute nitric acid. The zinc nitrate may easily be prepared by dissolving zinc in nitric acid until the acid is saturated. Other zinc salts may also be used when acidified with nitric acid.

A dipping bath which contains copper in solution from previous operations will not suit for articles which consist of zinc, tin, lead, antimony, bismuth, or their alloys, as these metals cause a deposition of copper upon their surface.

For small and medium sized articles the above solutions answer well, but with larger articles there are difficulties to contend with in consequence of the great bulk of solution required for immersion, and the size of vessels, which must be made of a material capable of resisting the action of acid liquids. For large and bulky articles a solution of potassium-ammonium tartrate may be used. This liquid has a weaker action on zinc than the ones mentioned before, but dissolves its sub-oxide.

The solution is prepared by dissolving $\frac{1}{2}$ lb. of cream of tartar in a pint and a half of water, adding ammonium carbonate till all effervescence ceases, then adding another 700 grains for excess. The solution is put on the articles with a brush, left on some time to act, then well rubbed in with a sponge, brush, or rag, which has been dipped in a mixture of whiting and water. Lastly, well wash with water. If the article is exposed to the air it soon oxidises, so that it should be plated or coloured as soon as possible after cleaning. Small articles may be kept from oxidising by immersion in a solution of potassium-ammonium tartrate, but large articles, if they cannot be immersed, should be rubbed with a clean cloth till dry.

§ 48. (3) **Silver.**—Silver is not oxidised like base metals by contact with moist air, but in the presence of sulphuretted hydrogen is readily coated with a film of silver sulphide, varying from yellow to black, according to the thickness of the film. Very often the tarnish assumes iridescent colours. This film of sulphide may be removed in several ways. Adhering dirt and grease is displaced as described for copper and its alloys.

Tarnish may be removed by immersing the silver articles in dilute sulphuric acid (1 : 5), or by boiling in a solution of 1 part cream of tartar and 2 parts common salt. Silver sulphide is readily soluble in potassium cyanide, and in sodium thiosulphate, so that when a tarnished silver article is rubbed with a cloth which has been dipped in a solution of either of these salts it is rendered perfectly clean. A 5 per cent solution of potassium cyanide and a 30 per cent solution of the thiosulphate is a convenient strength for the purpose.

Small articles may be immersed in a saturated solution of borax, in contact with a piece of zinc, when the surface after a time becomes very clean. The dull surface may be made bright with the scratch-brush, to be afterwards described.

§ 49. (4) **Iron and Steel.**—Articles of iron and steel after the removal of adherent dirt and grease, in the same manner as that described for copper, etc., may be cleaned by immersion in a mixture of lamp-black and concentrated nitric acid, washing with water, dipping in a soda solution, then well swilling with water, and drying out in sawdust.

For cleaning iron articles generally a cold mixture of about twenty measures of water, and one of sulphuric acid, is frequently used; but a better liquid is composed of one

gallon of water, one pound of sulphuric acid, with one or two ounces of zinc dissolved in it; to this is added half a pound of nitric acid. This mixture leaves the iron quite bright, whereas dilute sulphuric acid alone leaves it black, or of a different appearance at the edges. It should be scoured with sharp sand and brushed with a steel scratch-brush.

For glassy patches upon cast iron (which usually consist of iron silicate) hydrofluoric acid is used; it is kept in a bottle of gutta-percha closed by a bung of india-rubber; it must not be allowed to come in contact with glass vessels, nor must the mouth of the bottle be left open. The fumes from it are extremely dangerous to inhale. If a drop of it falls on the hand it should be thoroughly washed off at once, as it produces ulcers, and causes great pain after a few hours.

Articles of iron and steel which have been cleaned in acids, and the adhering acids washed away with water, may be protected from rusting by continued immersion in lime water, a solution of caustic soda, or water containing any caustic alkali, until required.

Articles of polished steel are cleaned in a moderately strong solution of potassium bisulphate. The article is immersed in the solution in contact with a piece of clean zinc. The zinc decomposes the solution with the liberation of hydrogen gas, and the steel is allowed to remain in the bath until the oxide of iron or rust is removed. Steel may also be cleaned in a 20 per cent solution of hydrochloric acid.

§ 50. (5) **Lead, Tin, and their Alloys.**—These metals are cleaned to remove dirt and grease, as with other metals, by means of caustic alkali solution, and brushing with

sand, etc. After another dip and well swilling in clean water they are ready for the colouring process without resorting to an acid dip.

§ 51. (6) **Aluminium.**—Articles of aluminium are cleaned in very dilute solution of potash, when the surface assumes a bright appearance; wash well with warm water and dry with a warm cloth. Aluminium alloys are treated like copper alloys.

B. MECHANICAL TREATMENT

§ 52. If the articles are not to be bronzed while in a crude state, which is rarely advisable, the mechanical treatment consists of imparting to them a more uniform surface by scratch-brushing, or a smoother and more lustrous one by grinding and polishing. But scratch-brushing is not only a part of the preparation of metals for bronzing, since it is employed alternately with dipping in the process of bringing out the desired tone of colour. After the first dip in the bronzing solution, a uniform tint is rarely attained, but after scratch-brushing one or more times with alternate immersion in the solution a much better result is achieved.

Scratch-Brushing.—Scratch-brushing may be achieved either by hand or by means of a lathe. A scratch-brush is merely a bundle of fine and hard brass or steel wires, about 6 or 8 inches long, according to the nature of the metal to be operated upon. The wires are of various degrees of fineness, and are also annealed to different degrees of hardness, to suit the various kinds of work.

Scratch-brushes must be carefully used, and their wires kept in good order. When they become bent they have

to be straightened by drawing the brush, held in a slanting position, several times over a sharp grater such as is used for grating nutmeg; or they may be beaten with a wooden mallet upon a small block held between the knees so as not to produce a dead stroke. By this means the wires become disentangled and straightened out.

Scratch-brushing by hand is a very slow and tedious operation, and only adopted for delicate work, or to get into crevices which cannot be touched by a revolving brush. The revolving scratch-brush is most generally used. It is much more rapid in its action and more effective. For very delicate objects scratch-brushes are made of spun glass, the fibres of which are very fine and elastic.

Scratch-brushes, if kept too long in water, become hard. When greasy they are cleaned in caustic potash solution. Oxides are removed from brass wire by means of aqua-fortis. This latter operation may be used for diminishing the size of the wires and making them smoother.

For making a good hand scratch-brush, choose a bundle or coil of brass wire of the proper thickness, and wrap a good string tightly around it for about two-thirds of its intended length, say about 8 inches long, then with a sharp steel chisel cut the bundle of wire close to the string at one end, and at 2 inches from the other end of the string wrapping. Dip the end closed by the string into a neutral solution of zinc chloride and plunge it into a molten alloy of tin and lead (soft solder), which solders all the wires and prevents their separation and injury to the hand of the operator. The brush is then fixed to a thin wooden handle. Very small scratch-brushes are necessary for reaching small parts and cavities. An old scratch-brush,

the wires of which have been bent in every direction, is useful for rubbing the insides of certain articles such as vases.

The ordinary circular scratch-brush consists of a round wooden frame, into the periphery of which is placed bundles of wires at regular intervals. A hole is left at the centre for fixing it on to the revolving spindle of the lathe.

For cleansing purposes a circular scratch-brush, which the workman can readily refurnish with new bundles of wire, is preferable. It consists of a round iron disk about one-tenth of an inch thick and about 6 or 7 inches in diameter, provided in the centre with a hole for fixing on the spindle of the lathe. At the distance of from one-fifth to one-fourth of an inch from the periphery of the disk, holes of about one-tenth of an inch are drilled at a distance of an eighth of an inch apart. Through these holes are drawn bundles of wire about 4 inches long, so that they project an equal distance on both sides. Then the bundles are bent towards the periphery, and on each side of the iron disk a wooden disk one quarter of an inch thick is placed. The periphery of the wooden disk, on the side next to the iron disk, should be turned semi-annular, so that the wooden disks, when secured to the spindle, press very lightly on the wire bundles, and the latter remain very mobile.

When the compound brush is fixed on the lathe and made to revolve rapidly, the bundles of wire, in consequence of centrifugal force, stand rigid, but being mobile will give way under strong pressure without breaking off. It should be remembered that only the sharp points of the wires are effective, so that by putting too much pressure

on the brush the wires are bent without securing any advantage as regards smoothing.

Scratch-brushing is seldom done dry; the brush and work must be constantly wetted with a liquid which carries away the impurities and makes the wires not too harsh. The liquids employed to assist the brushing are various; such as water and vinegar, or sour wine, stale beer, etc., or solutions of cream of tartar or alum. A solution of sodium carbonate may also be used.

Lathe brushes are mounted on the spindle of the lathe, and over the revolving brush is fixed a wooden box, lined with zinc or lead, and open only at the front, which prevents the liquid splashing on the workman. On the top of this box is a reservoir for holding the liquid for wetting the brush, or it may be contained in a tank fixed to the wall, or in any convenient position above the latter. In the top of the box and floor of the reservoir is fixed a small pipe terminating in a tap, which is fixed over the centre of the brush, by this means the stream of liquid may be regulated to the desired amount. In the bottom of the box is another hole connected with a pipe to carry off the waste liquid. As this may be used over again several times it is usual to have a pipe of flexible material, and dipping into a large stone jar, from which the top reservoir may be filled as often as necessary. In working the lathe the top of the brush is made to revolve towards the operator, who holds the objects to be brushed at the bottom. After scratch-brushing every trace of the lubricating liquid must be washed away before placing or replacing the objects in the bronzing bath.

§ 53. **Grinding and Polishing.**—Wherever possible it is advisable to have articles or parts of articles highly polished

before bronzing. But polishing imparts some grease and dirt which would prevent the bodies taking the bronze uniformly, so that they have to be dipped in potash or other cleansing liquid and swilled before putting into the bronzing solution. Polishing is generally done at a lathe set in motion by steam power.

When it is necessary to remove a very rough surface the objects are ground on an emery wheel. This is a wooden wheel covered with a thick strip of leather on its edge, which is coated with emery powder of different degrees of fineness. A much better plan, and one which is coming into general use, is to have these wheels or "bobs," as they are termed, made entirely of leather and faced with emery powder. The bobs have holes in the centre by which they are fixed on the lathe.

Polishing bobs are made from walrus or hippopotamus hide in a great variety of sizes to suit all kinds of work; some are made from bull-neck leather, felt, etc. Three different grades of emery are generally used—No. 60 to 80 for preparatory grinding; No. 120 for fine grinding; and flour emery for imparting a finish. The bobs thus coated are termed respectively, "roughing," "medium," and fine bobs. In most cases a circular revolving bristle brush may be substituted for the last grinding, the articles being moistened with a paste of oil and fine emery.

Care must be taken not to execute the brushing or the fine grinding in the same direction as the previous grinding, but in a direction at right angles to it. The coating of the roughing wheel with emery is effected by applying glue and then rolling it in the dry emery powder. When the first coat is dry a second is applied, and finally a third. The wheel is then dried in a warm place. Before use the

revolving bob is greased with tallow and the inequalities removed by pressing a smooth stone against it. The rough grinding is generally done dry, but in fine grinding the objects are often moistened with a mixture of oil, tallow, and emery, of the same degree of fineness as that on the bob.

A polishing lathe consists essentially of an iron frame or support with two sockets or bearings at the top, in which works the revolving spindle which carries the brushes. A usual form of spindle has two pulleys between the bearings arranged at its centre (fast and loose) and the two free ends screwed taper-wise so as to fit various sized holes in the bobs, and to keep them always rigid, since the motion tends to make them travel towards the wider parts of the screws, and the more the pressure the tighter they become. Such a lathe may be driven by power or by manual labour. The former is usually employed, and for large work is absolutely necessary. The spindle is made to revolve at very high speeds. The lathe just described is arranged for two bobs, one at each end of the spindle, so that two men can work at the same lathe at the same time.

§ 54. Polishing as distinguished from grinding is employed to impart a highly smooth surface and brilliant lustre to goods before plating and bronzing, and also in some cases to give a final finish after these operations. The bobs are made of a large number of circular pieces of felt or calico from 9 to 12 inches in diameter placed together, having a hole in the centre to fit the spindle of the lathe on which the bob has to be fixed. A circular piece of stout leather or metal about 3 or 4 inches diameter, with a similar hole at the centre, is fixed to each side of the bob; these serve to bind the pieces firmly together by driving

four pins through the whole, each pin having a head on one side and riveted on the other. These bobs vary in width from 3 to 5 inches. It is very important that a bob should be properly centred, otherwise it will not revolve circularly.

When a new bob is made it is necessary to dress the rough edges of the disks of cloth by making the bob revolve on a lathe and holding a sharp knife against the edge in a fixed position; this also helps to make the balance true by shearing off any inequalities.

Two of these bobs are employed to produce a final polish on brass and metal generally. The first one is used with oil and powdered rottenstone, or the bob may be greased with a little tallow and then "tripoli" rubbed on. This is termed the "grease" bob. The second one is known as the rouge or finishing bob. A piece of lime is first held against the revolving bob and then a bar of rouge, when the articles may be finally polished. The lime prevents the rouge sticking in parts and enables the metal to be uniformly brightened. Some polishers use a paste of powdered rouge mixed with water, and a very little oil instead of the bar rouge, which is a mixture of rouge, melted wax, and a little tallow, cast into moulds with the use of strong pressure.

PART III

CHEMICAL METAL-COLOURING

§ 55. By this term is understood the production of a thin but firm and compact coating on metals by chemical means. As already stated, the metals differ in colour among themselves, and a great variety of shades may be obtained by suitable alloying, so that the deposition of a metal or alloy upon another metal is, strictly speaking, metal-colouring; but if the whole subject of electro-deposition of metals were to be included in the present work, it would go beyond the intention of the author and the legitimate scope of the subject, especially as there are several excellent manuals of electro-metallurgy already in existence, from which abundant information relating to that branch of art may be obtained.

But a work on metal-colouring would be very incomplete without embracing certain methods of metal-deposition, because the two subjects are so intimately associated that one cannot be treated without some reference to the other. It frequently happens that electrical action is an important aid to the production of a certain colour, and in all cases where such an aid is useful it will be fully described. For example, a very thin

coating of nickel on a brass article will modify the colour when it is put into a bronzing solution.

COLOURING OF COPPER

§ 56. The colours ordinarily produced on copper articles by means of bronzing agents chiefly depend on the formation of oxygen and sulphur compounds, by which the surface is changed into cuprous oxide Cu_2O, cupric oxide CuO, or cupric sulphide CuS respectively.

Cuprous oxide is capable of existing in different modifications as regards colour, producing various shades, from bright red to brownish-black, according to its physical condition and the thickness of the deposited film, which, as is well known, alters the particular shade of colour. Cupric oxide, according to its thickness, varies from brown to brownish-black. Whatever the natural colour of the compound deposited or produced on a metal, the tone will be modified by the colour and physical condition of the base, except when the film of the deposit is of such a thickness as to completely hide the base, or of such an opaque character as to completely obscure it.

Bronzes, like pigments, vary as to opacity and transparency, and it will readily be understood that a transparent or semi-transparent film on a metal such as brass will produce a very different effect to a similar film imposed on copper. Advantage is therefore taken of these facts to produce different colours with the same chemical reagent. In like manner sulphur compounds may be made to assume various shades of colour when deposited on copper and its alloys, varying from a pale brownish-yellow to brown and brownish-black, and also from grayish-black to

a blue-black. If now we employ a combination of these bodies (oxides and sulphides) it will at once be understood that a still greater variety of tints may be obtained. Copper therefore may be coloured from a pale bronze tone to a deep brownish-black or deep bluish-black by the above-mentioned agents.

Copper is also coloured by the action of basic copper carbonate, or basic copper chloride, by which the antique patina is produced in different shades of green. There is no other metal which, by the agency of its own compounds, can be so variously and so easily coloured as copper if the conditions of its combination with oxygen, sulphur, carbonic acid, and chlorine are properly understood. Copper is gradually oxidised, even at the ordinary temperature, either in dry or in moist air, if carbonic acid is present in sufficient quantity. If carbonic acid is absent, and the temperature of the air is suitably raised, or if the copper is heated, then combination of copper and oxygen occurs.

If copper is heated to redness it becomes first pale yellow, then red, then violet, by the formation of cuprous oxide Cu_2O, and finally receives a black film, which on the outside is cupric oxide CuO, but on the inner surface, which is in contact with the copper, a deep red film of cuprous oxide is produced. When a certain thickness is attained, this scale falls off, especially if the heated copper is plunged into cold water. Copper can therefore be coloured by heating, due to the formation of one or both of the above oxides.

§ 57. Buchner states that by suitably operating on copper, so as to produce layers of oxide of different degrees of thickness, the well-known colours of thin plates are exhibited in definite order, each colour varying with the

wave-length of the light. Steel and cast iron, when treated in a similar manner, show the colours yellow, red, violet, and blue to sea-green. Five bands of colours are produced. In the first band are pale, clear, and dark yellows, light blue and sea-green. In the other bands the colours are nearly the same. In the last colour scale, produced at the highest temperature, red and green are distinctly brought out. These colour bands are attributed to interference, as in the case of Newton's rings, which are formed when a lens of small curvature is pressed on a plane parallel plate. It is important for the action in this instance that the colour bands exhibit different breadths. Experience has shown that a colour which appears lighter in the air is more permanent, and furnishes a wider band in the colour scale.

The colour depends on the degree of temperature and on the duration of the operation, so that with a high temperature and a short exposure the same results may be achieved as by using a lower temperature and a long exposure. The latter, however, is generally preferable, as the film of oxide is more firm and durable. There seems to be a certain limit of temperature, which cannot be exceeded, for the production of every shade of colour.

But air contains bodies other than oxygen, and when articles of copper or its alloys are exposed to moist air the carbonic acid and oxygen both combine to form basic copper carbonate (often incorrectly called verdigris), termed antique bronze. In general it may be stated that the colours will be more beautiful the longer the articles have been exposed to atmospheric influences.

Concerning the antique bronze two different kinds exist—(*a*) The one produced on copper in air, as men-

tioned above, and having a bluish-green colour; (*b*) the other produced on copper articles which have been buried in the earth in contact with saline bodies, by which a yellowish-green patina or incrustation is formed, consisting generally of basic copper chloride, especially when the copper has been deeply buried.

Copper articles may be coloured easily and rapidly by heating with certain compounds, such as iron oxide. They may also be bronzed quickly by immersion in certain acid, alkaline, and neutral solutions, such as copper sulphate, copper nitrate, etc. The colouring will also in these cases depend on the temperature, strength of the solution, and time of exposure or immersion.

VARIOUS SHADES OF BROWN COLOUR ON COPPER

COLOURING COPPER BY DRY METHODS

§ 58. This method of colouring copper is largely employed, the general view being that oxygen containing bodies, when applied to copper in the form of a paste, and the whole heated, effect a chemical change whereby some of the oxygen of the applied oxide is given up to the copper with the production of the lower oxide of copper, which, as is well known, has a red colour.[1] It has been stated before that this oxide is capable of existing in a variety of modifications as regards colour, so that numerous shades may be obtained by its production, varying from bright red to dark brown.

It should be remembered what has been said with regard to the necessity of having the articles to be bronzed

[1] See § 71, p. 112.

scrupulously clean and as highly polished as possible, because on this necessary polish will the uniformity of the colour largely depend.

§ 59. **Treatment with Iron Oxide at the ordinary Temperature.**—(*a*) Reichardt states that when highly polished copper articles are rubbed for some time with a piece of leather and very finely powdered red iron oxide a high lustre and a dark brown colour result, due to the chemical action occurring between the iron oxide and copper. One part of oxygen leaves the iron oxide and goes to the copper, forming cuprous oxide, which, by the constant rubbing, passes into the pores of the metal. That this action occurs is open to very considerable doubt. I have not been able to produce the effect in this way. Possibly by uninterrupted rubbing for a considerable period of time a moderate change might take place, but no one would trouble to expend such enormous labour for such an insignificant result when the same end may be achieved much more effectually with comparatively little labour, and in a small fraction of the time, by help of a moderate amount of heat. It may be taken as settled that no good result has ever been achieved by the action of oxide of iron on copper at the ordinary temperature, as the author has proved by a long series of experiments, in some of which the bodies were allowed to remain in contact with each other for ten to twelve days with but very little change taking place. All the experiments were quite barren of good results, the only consolation being found in the assurance that no satisfactory bronzing is possible by this means; and it is hoped the experience may be useful in preventing others wasting valuable time in the effort to attain a good colour by this means.

(*b*) The following method among others was adopted in the above-mentioned experiments. Five parts of the red oxide were thoroughly incorporated with 8 parts of graphite, and the mixture made into a paste with a little alcohol :—

5 parts red iron oxide (Fe_2O_3).
8 ,, graphite.

A thick layer of this paste was put upon the copper articles, which were allowed to remain untouched for from one to twelve days. The paste was then removed with a woollen cloth and the copper well brushed with a moderately soft brush. The experiments were complete failures.

(*c*) The experiments were then tried with the addition of heat. The articles were covered with the paste of iron oxide, graphite, and alcohol, and allowed to remain on a hot iron plate at about the temperature of a lacquering stove for a time varying from five minutes to an hour or more, and then the paste removed and the object brushed as before. The articles were coloured very unequally, and only after repeated operations with the same article could any thing like uniformity be achieved.

(*d*) By well rubbing copper with wax or fat and heating, then rubbing it off with a rag, and well brushing, a nut-brown colour is said to be obtained. Here again a great many repetitions of the process on the same metal were tried, but with no good results. Doubtless, if any one cared to repeat the process a sufficient number of times some sort of colour would be obtained, depending on the nature and continuance of the heating. At the best the method is only suitable for small articles, and these are

just the things which can be done better and more rapidly in other ways.

(*e*) The following process has also been recommended for giving a uniform colour on copper :—Warm the copper to about 100° C., *i.e.* to the temperature of boiling water, rub on it a little moist rouge, and brush with a plate brush until it receives a uniform colour. Repeat the process until the desired colour is attained. The iron oxide is removed from the surface of the copper by pouring over it a saturated solution of copper acetate, and the metal is then dried by rubbing with a woollen cloth. This process is very defective, as it requires an enormous expenditure of labour for very little result, and is open to the same objection as the preceding one.

(*f*) A good result is obtained in the following way, according to Langbein, by which shades varying from light to dark brown may be obtained :—Take two parts of red iron oxide and one part of blacklead, make them into a paste with water or alcohol, paint the article with the mixture, place it in an oven or on a hot plate. Remove the baked powder when thoroughly dry and well brush the metal as before described. The darker the desired colour the longer must the metal be heated and the higher must be the temperature. If the colour is not deep enough, or, what is very likely, not completely uniform, the operation must be repeated. The metal should be finally rubbed with a little alcohol and brushed with a soft brush till dry. A finish may be given by brushing with a soft brush which has been previously rubbed on pure wax. The oxidising paste must not be too thin, especially when the higher temperatures are employed. It is always safer to heat for some time at about 100° to 150° C. than to

employ a higher temperature, as the higher the temperature the less uniform will the colour be likely to be.

(*g*) The following experiments were performed to test the value of this method:—(*a*) A piece sheet copper, (*b*) an electro-coppered ash-tray, (*c*) an article made of commercial cast copper, were covered with a thick paste and heated on the plate of a lacquering stove for some time. They were then cleaned with a soft brush and alcohol, then finished with a waxed brush; (*a*) became shellac-brown in colour, (*b*) chocolate-brown, (*c*) a lighter brown. The operation was repeated several times. Electrolytic copper takes the colour readily under the above treatment, cast copper less readily, and sheet copper very slowly. As a rule, the more quickly the desired shade of colour appears with moderate heating the more beautiful it is.

§ 60. A bronzing paste is said to be made with a mixture of copper tartrate, red iron oxide, bone-ash, and water. The article to be bronzed must be coated with a thick layer of the paste, then heated over a fire till dry, and brushed with a soft brush exactly as directed in the previous method. The operations must be repeated to obtain a uniform colouring. The proportions recommended are—

1 part of red iron oxide.
2 parts of a mixture of the other ingredients.

The heating must be done very uniformly or the metal will be of a darker colour in the parts most strongly heated. In our experiments electro-deposited copper received a dark brown colour, which became darker with a repetition of the process. Cast copper took a light brown. With sheet copper no good result was obtained. The

method is very inferior to the preceding one, and cannot be recommended.

§ 61. **English Method.**—Red iron oxide is made into a paste with water to the consistence of cream, and this is painted over the article with an ordinary paint-brush. It is then heated over a fire, or, better still, in a muffle, or on a hot iron plate at a moderate temperature, until the paste is thoroughly dry. After allowing to cool the powder is removed with a soft brush (a painter's dust-brush) and then, if not a finished article, it is beaten or hammered. Or the copper article with its coating of iron oxide is held over a wood fire into which some pieces of coal are placed. By means of the smoke a deposit forms on the article, and when this soot begins to be dissipated by the heat the metal is considered to be sufficiently heated. It is very important to keep it at a uniform temperature, and not to allow it to get too hot, or the bronzing will appear patchy, and the metal require to be thoroughly cleaned again and the operation repeated.

On testing this method with a stamped-brass tray which had previously been electro-coppered a good nut-brown bronze colour was obtained. Another similar tray, with a much thinner coating of copper submitted to the process, gave unsatisfactory results. In succeeding experiments with stamped and cast work, with good coatings of copper, results equally good with the first were obtained. The cast work took a paler shade of colour. Some were coloured a deep gold colour, others were of a brick-red shade. These results were probably due to insufficient heating.

From these experiments it may be inferred that red iron oxide is quite sufficient to effect the desired change

of colour without the addition of graphite and other bodies. They also showed that the article must be thoroughly clean and polished as highly as possible before the application of the bronzing paste, that a sufficiently high temperature is required, and that all parts of the object must be uniformly heated. As a general rule two or three repetitions with scratch-brushing between is much more effectual than one operation alone. They prove what we have frequently observed with immersion processes also, that a too thin coating of copper is soon corroded and removed, leaving a surface of brass in places and vitiating the result. This method is one of the very best for producing a dark brown colour on electrotypes. Haldane states that in preparing medals for the Melbourne Exhibition, a rich chocolate colour was obtained by the addition of a little copper acetate, mixed with an alkaline sulphide, to the ordinary iron oxide bronzing paste by which a film of mixed copper oxide and sulphide was produced.

§ 62. **Chinese Method.**—According to several authorities the Chinese use a mixture of—

2 parts copper acetate.
2 ,, cinnabar (HgS).
5 ,, ammonium chloride.
5 ,, alum.

The salts must be finely powdered and made into a paste with water or vinegar. This is pasted over the copper article in the usual way, and then heated for some time over a fire or on a hot plate. In case of large hollow vessels glowing coals are placed inside to raise them to the requisite temperature. After cooling, the vessel is well washed, dried, a fresh coating put on, and

the operation repeated until the desired colour is obtained. The addition of some copper sulphate is said to make the colour darker, and borax to make it more yellow.

As the result of a number of experiments with this mixture in the above proportions we found that the mercury sulphide was decomposed, producing a black deposit which could not be completely removed, and on washing off the powder before heating, the copper was observed in every case to be coated with a deposit of mercury. The metal was eaten away so much that the design was partly destroyed and no useful colour was attained. Therefore the method, using the ingredients in the proportions mentioned, is quite worthless. It was thought that the failure was due to excess of mercury sulphide, but on making the mixture very dilute, and also by reducing the quantity of mercury sulphide to one-tenth, the same unsatisfactory results were obtained.

§ 63. The following mixture is recommended by Langbein for the production of a brown colour :—

1 part potassium nitrate.
1 ,, sodium chloride.
2 parts ammonium chloride.
1 part of liquid ammonia.
95 parts of vinegar.

The solution is painted on to the article, allowed to dry, and the article then vigorously brushed. Or the brushing may commence when the article is still wet and continued until it is dry.

No good results were achieved by the author with this mixture, although the experiments were repeated several times, and the proportion of the ingredients were varied, as well as the methods of applying them to the

work. Electro-deposited copper, cast copper, and sheet copper were immersed in the solution, and, without rinsing, were put on a hot plate, and left there until a brown colour appeared; but the surface was disfigured with black patches. The processes were repeated seven or eight times without any better results. Simple pickling had no appreciable effect. The best colour was obtained by dipping in the solution, and then heating on a hot plate without previous swilling. No good colour was secured by heating the article before immersing in the solution. When the work was pickled and heated on the hot plate, then reimmersed in the solution, the brown colour produced by the heating disappeared. Scratch-brushing does not appear to facilitate the process.

Langbein states that a warmer tone is produced by the method adopted at the Paris Mint, which is as follows:— Powder and mix intimately equal parts of copper acetate and ammonium chloride. Take a large tablespoonful of this mixture, boil it with water in a copper kettle for about twenty minutes, and pour off the clear fluid. To give copper a bronze-like colour with this fluid, pour part of it into a copper pan, place the objects separately in it upon pieces of wood or glass so that they do not touch each other, or come in contact with the copper pan, and boil them in the liquid for a quarter of an hour. Then take the objects from the solution, rub them dry with a linen cloth and brush them with a waxed brush to finish. This would more correctly be described under the head of wet methods, but it has been thought advisable to introduce it here to show the uselessness of a complicated mixture, when a much simpler one is quite as effectual. In the author's experiments with this method, copper

articles were coloured terra-cotta. On heating they assumed a deep reddish-brown. Much better methods are given under the head of Wet Colouring.

§ 64. Dienst states that a very beautiful brown colour, unaltered by moderate heat, is obtained from the following mixture :—

1 part by weight of neutral copper acetate.
1 ,, ,, ,, ammonium chloride.
250 parts ,, ,, water.

The above salts are dissolved in the water, and the copper articles are painted with the solution. They are then heated over a coal fire until the green colour turns to a copper colour; then besmeared again with the solution, which should, however, be more dilute than in the first coating; heated again over a fire and the operation repeated as often as necessary till a uniform colour of the desired dark brown shade is obtained.

In testing this method a light brown colour was obtained, but not very uniform or of a good tone. The colour also blackens by the action of sunlight.

It is stated that if the copper to be bronzed has been tinned the tin does not go into the solution, but after five or six repetitions the copper receives a brassy colour, which, after three or more repetitions of smearing and heating, changes to a splendid yellow. If it is desired to produce a brown colour the solution must not be painted on while hot, and with twenty to twenty-five repetitions a pale brown colour is obtained. When the desired colour is reached the metal is washed in clean water, dried quickly, and polished with waxed brush. The bronzed metal is then held over a low fire to make the colour deeper and more durable.

§ 65. A very beautiful and pleasing colour of a light brown shade may be quickly produced by a mixture of—

1 part copper sulphate.
1 ,, zinc chloride.
1 ,, water.

The above forms a paste which is applied to the article, and allowed to dry on it. It is then well washed with water, when a uniform colour is obtained. This would be one of the most valuable colours if it were permanent, but unfortunately it is changed by the action of light to a dark green, almost black. This change also occurs when the bronze is coated with a film of transparent lacquer, and although we have tried several methods of preventing the change, no suitable remedy has yet been discovered.

§ 66. The following mixture forms an excellent bronzing solution, and may be used for copper articles with or without subsequent heating :—Take

120 grains of copper sulphate.
½ pint of water.

Boil the water until the copper sulphate is dissolved, neutralise the solution with sodium hydrate, then add 150 grains of red iron oxide. Now immerse the copper articles in the turbid solution, take out and heat on hot plate. Repeat the operation until a reddish-brown colour with a violet tint is obtained. The violet tint can only be observed in full daylight. Electro-deposited copper received a full and rich reddish-brown colour, and cast copper a lighter brown. These beautiful colours become darker in tone by more heating.

This solution gives good results both on copper and brass by immersion only, without the addition of heat, but the

colour is not of that deep rich tone which is secured by subsequent heating. The best effects are obtained after the process has been repeated once or twice. The results achieved by heating over a charcoal fire were found to be most effective.

§ 67. A solution similar to the former one, with the omission of iron oxide, produces very good colouring effects, but the colours are paler in tone. Take

120 grains of copper sulphate.
9 fluid ounces of water.

Boil and add strong sodium hydrate solution until a precipitate sufficient to render the solution turbid is formed. Immerse the articles and treat them as in former method.

§ 68. Another bronzing paste which is said to give very good colours, of a pale to dark brown shade, is made by mixing basic copper sulphate with water and coating the article with a thick layer, then heating as usual. The mixture for testing the method was made in the following way: —(*a*) 100 grains of copper sulphate were dissolved in water and copper hydrate precipitated by the addition of a solution of sodium hydrate; (*b*) the copper hydrate precipitate was filtered off and mixed with 100 grains of copper sulphate and made into a paste with water. The paste was thickly smeared over the work, which was then heated over a charcoal fire. Electro-deposited copper received a light brown or dark chestnut-brown colour according to the degree of heat. Better effects were obtained by repeating the process once or twice. The residue left on the work after heating is somewhat difficult to remove, and it is difficult to obtain a perfectly uniform colour over the whole surface. The method given in § 66 is much preferable to this one.

§ 69. Walcker recommends the following mixture which has been tried by the author with the results recorded below :—

Ammonium carbonate . . .	300 grains.
Copper sulphate	150 ,,
Vinegar	5¼ fluid ounces.

Evaporate the solution to dryness, and then add—

Vinegar	5¼ fluid ounces.
Oxalic acid	4 grains.
Ammonium chloride . . .	16 ,,

The mixture is boiled and the residue filtered off. The article is warmed and the solution painted on the work. Then boiling water is poured over it, and the surface rubbed, first with an oiled pad, then with a dry pad.

(*a*) Brass ash-tray, oiled and wiped dry, as recommended above.
(*b*) ,, ,, dried in sawdust only.
(*c*) Coppered ,, oiled and wiped dry.
(*d*) ,, ,, dried in sawdust only.

The above trays were immersed in the filtrate only.

It was found that immersion was much better than painting on the solution. The wiping with oil removes some of the bronze colour, unless done very softly indeed.

The colour produced on brass is distinctly yellowish-green, while the colour imparted to copper is similar to that produced by copper cloride (§ 73), and blackens by exposure to light.

(*a*) darkens slightly in diffused daylight; (*b*) appears not to change; (*c*) darkens slowly, probably because the bronze has been largely wiped off by the oiled rag; (*d*) darkens very quickly in daylight.

The residue left on the filter was rubbed into a paste with a few drops of the filtrate, and painted on the work to be bronzed, which was then heated on a lacquering stove. After the paste was thoroughly dried it was washed off with boiling water. Brass received the same colour as by the immersion method, but the colour was not quite so uniform. Copper assumed a deep brown colour, which became darker on exposure to light. This process might do for work that is too large for the immersion method.

§ 70. A method similar to the above has also been recommended, using a mixture of—

Ammonium chloride . . .	460 grains.
Potassium oxalate	150 ,,
Vinegar	9 fluid ounces.

The above salts are to be dissolved in the vinegar, and the metal to be immersed in it, or the solution painted on the warmed article, using a soft brush. It may also be rubbed on with a soft linen rag.

We found that the colour produced on copper after the lapse of a considerable time was the same as that given by copper chloride solution. The liquid is quite inoperative at first, but it becomes green after a time by dissolving some of the copper, so that it would save time and trouble by adding some soluble copper salt at the commencement. Rubbing the solution on to the work appears to hasten the reaction, but the method is very tedious. But dipping the work in the solution, draining off the excess, drying on stove, rinsing in water, and drying out in sawdust, is a quicker method than rubbing only with wet and dry pads respectively. Neither of the

methods is, however, effective till the solution becomes charged with copper, as stated above.

§ 71. From observations made during the various experiments on bronzing with a paste of oxidising material, such as iron oxide, the author felt convinced that the usual explanation was not the correct one. Most authorities state that when copper is covered with a paste of red iron oxide and moderately heated (say to 150° C.), that the red oxide Fe_2O_3 changes to the black oxide Fe_3O_4, giving up oxygen which unites with the copper, forming the red copper oxide Cu_2O. For this reason graphite is usually mixed with the iron oxide to effect the reduction.

It is well known that red iron oxide prepared by decomposing iron oxalate is converted into the black oxide by heating to 350° C. in a current of hydrogen. Carbon monoxide will produce the same effect, but requires considerable time. At a higher temperature solid carbon can effect the same change, but the action is exceedingly slow. Hence it may safely be inferred that no oxidation of copper by iron oxide at the temperature admissible for bronzing can take place.

In order to show that the oxidation of copper, when coated with a paste, does not proceed from the paste itself but from the oxygen of the air, a paste was made with finely powdered fluor-spar and water, with which a coppered article was covered in the usual way. This was then heated till the paste was well dried (about fifteen minutes), then it was washed off and the copper was found to be darkened. The article was scratch-brushed, and again covered with the paste and reheated. When the paste was removed a beautiful brown colour was

found on the surface exactly as when the iron oxide paste was used. This shows that the paste simply acts mechanically in limiting the supply of oxygen to the copper, with the consequent formation of the red oxide, or a mixture of the red and black oxides, in which the former predominates.

LIGHT BROWN COLOURS ON COPPER

Colouring Copper by the Wet Way

§ 72. This method of colouring metals presents many advantages over the dry way, both as regards economy of time and uniformity of results, since the articles are completely immersed in the same medium, practically at the same temperature in all parts, and equally exposed to the same influences, always provided that the metal is made scrupulously clean in every part before being suspended in the bronzing solution.

Any inequalities as regards the physical condition of the plain parts will not be removed, but rather intensified by the operation, so that such parts should be highly polished and scratch-brushed to remove this unevenness before the final cleansing. With every precaution it often happens that inequalities are revealed after the first dip, but these are generally removed by a good scratch-brushing after well swilling in water.

It might be supposed that the stronger the solution the more effectual it would be in effecting a desired change of colour, and in some cases this is true, since the chemical action is retarded by diluting the solution. But there are other considerations to be kept in view. It

must be understood that a bronzing solution is, in its very nature, corrosive, and if the corrosive action is too rapid, not only is the colour patchy, but the metal is pitted with holes, due to the unequal action of the salts on the surface of the metal or alloy. Moreover, when a solution is too concentrated the salts crystallise on the surface of the suspended article and become baked on, as it were, by the heat, and make it exceedingly difficult to remove them without much scratching, which destroys the coloured surface, and necessitates beginning the operation over again.

It may be taken as a rule that dilute solutions are necessary, not only to prevent undue corrosion of the metal, but also to keep the salt in solution by the excess of the solvent, which is generally water. Strong solutions give a deeper tone than weaker ones, so that for the lighter tones of colour dilute solutions are necessary. It is sometimes necessary to pour the solution over an object when the latter is too large to be suspended in the bath, and in such a case it is still more important not to have the liquid too strong, as the tendency of the salt to crystallise on the work is greater in consequence of the cooling effect of the air and of the article. In such cases a dilute solution poured over the body several times is much better than a saturated solution poured over it fewer times. In bronzing, as in many other things, "slow and sure" is an excellent motto. Of course the solution may be made so dilute as to have no effect on the metal, in which case more of the salt must be dissolved in it; or a solution may have been used so much as to become exhausted, in which case a fresh liquid should be prepared.

The beginner, however, should satisfy himself that the solution is exhausted before throwing it away. It frequently happens, especially when boiling solutions are used, that the salt is deposited at the bottom of the vessel in consequence of the evaporation of the water or other solvent, a sufficient amount of that liquid not being present to keep the bronzing agent in solution. In such a case more water should be added and the contents of the vessel well stirred while the liquid is kept simmering.

When a solution is being made or an old one being revived care should be taken to see that all soluble matter is dissolved, and that the liquid is allowed to stand a sufficient length of time afterwards to enable the insoluble suspended matter to settle, when the clear liquid should be poured into a clean vessel for use. It is sometimes necessary to resort to filtration, as certain ingredients are mixed together so as to form an insoluble precipitate, which requires to be removed from the soluble portion. Sometimes the precipitate is the substance required for use, but more often it is the solution which is most valuable. In either case they may be separated by filtration.

Several methods are adopted for separations of this kind. A bag of very fine muslin or calico is often sufficient, but the best way, when the precipitate is very fine, is to use a funnel, in which is placed white blotting-paper or filter-paper, which is specially prepared for the purpose, and may be obtained at chemists' shops.

Vinegar, which may be considered as impure acetic acid, is a solvent frequently used in making bronzing solutions. But commercial vinegar is often contaminated

with hydrochloric and sulphuric acids, and in the presence of these bodies bronzing often becomes impossible, or only partially successful, so that vinegar free from these ingredients should, if possible, be used. If mineral acids are added to vinegar, even in small quantity, an equivalent quantity of acetic acid is displaced. One part of sulphuric acid added to one thousand parts of vinegar is lawful, and is added with the idea that its presence prevents putrefaction, although it has been proved that the notion is erroneous. The presence of hydrochloric acid is rarer. English proof vinegar contains 6 per cent of acetic acid. It is better to work with a dilute solution of acetic acid containing 5 or 6 per cent of pure acetic acid, and thus avoid the defects arising from the use of adulterated vinegar.

In workshops and places where bronzing is conducted on a large scale the solutions should be placed and used under a hood connected with a chimney, so as to carry off the acid and other fumes. This is important for two reasons—(*a*) from a sanitary point of view, the fumes from many solutions being injurious when inhaled by the workman; (*b*) any finished work standing in the shop is very liable to be affected, and specks produced on the surface.

It is also necessary to work with clean vessels. When a vessel which has been used for a certain solution is required for one of another kind, much inconvenience and disappointment will be avoided by taking care to remove every trace of dirt from it before using it to prepare or to hold another solution.

If common water is used it should be examined to see that it is of good quality and free from many impurities

with which ordinary water is often contaminated. Spring and well water often contain considerable quantities of lime, magnesia, common salt, iron salts, etc., the presence of which may cause various kinds of separations in the bronzing baths. On the other hand, river water is frequently impregnated with so much organic matter that its employment without purification cannot be recommended.

Rain water, or better, distilled water, is the best for the preparation of solutions. However, rain water collected from metal roofs and gutters exposed to various fumes arising from works in large manufacturing towns should only be used with caution. Rain water should be caught in vessels of earthenware or wood free from tannin, and filtered. Where river or well water has to be used, thorough boiling and filtering before use is generally necessary in order to separate the carbonates of alkaline earths held in solution.

Another important factor is the purity of the chemicals employed for bronzing. Many failures arise from inattention to this point. Attention has already been drawn to the necessity of purity in vinegar, and many instances might be cited of imperfect results in consequence of using impure salts. Take caustic potash for example, it is likely to be contaminated with sulphuric and hydrochloric acids among other impurities. Ammonia may contain chloride, sulphate, and carbonate of ammonium. Acetates are liable to contain sulphates, etc.

§ 73. Before proceeding to give definite instructions for the preparation and mode of applying bronzing solutions suitable for copper goods, it will be well to discuss the chemical changes likely to occur in the various processes,

for it is as important for the operator to know what to avoid as to know what to search for.

It has been already explained that copper forms two compounds with oxygen, viz. Cu_2O, which is red, and is termed cuprous oxide ; and CuO, which is black, and is termed cupric oxide. Also copper forms two compounds with chlorine, viz. cuprous chloride Cu_2Cl_2, and cupric chloride $CuCl_2$ of various shades from white to brown. The same metal unites also with sulphur forming two compounds varying from brown to a deep bluish-black, termed respectively cuprous sulphide Cu_2S, and cupric sulphide CuS. There is also a pentasulphide, said to be formed by the action of potassium pentasulphide on copper sulphate, and having the formula CuS_5. Certain salts of copper, such as the carbonate and acetate, produce colours varying from pale to deep greens and bluish-greens.

Carlemann observed that a plate of copper exposed to chlorine gas till it becomes yellow, blue, red, yellow, and finally blue again, or treated with a solution of cuprous chloride in hydrochloric acid till it assumes a light brown tint, becomes so sensitive to light that photographs may be taken upon it, the parts on which the light falls turning black. The photographs, if kept in the dark, remain distinct for months, but ultimately fade.

According to Priwoznik, a solution of cuprous chloride does not produce this effect unless it has been partly converted into cupric chloride by the action of the air. He finds also that the best way to make a copper-plate sensitive to light is to dip it in a neutral and only slightly diluted solution of cupric chloride, and thinks it very likely that the sensitiveness is due to a thin film of cuprous chloride,

this compound in the moist state being known to become coloured by the action of light.

Alloys of copper with silver, manganese, and zinc, may also be rendered sensitive to light by similar treatment, but in a lower degree than pure copper; in fact, this difference of behaviour may be used as a ready means of testing the purity of copper.[1]

The action referred to in the above paragraph had been observed by the author before his attention had been directed to the work of the experimenters there mentioned, and in a large number of experiments with various solutions, in which a soluble chloride was present, the same light brown colour was obtained which invariably blackened on exposure to daylight, although gaslight appears to have no action.

Many unsuccessful attempts have also been made to fix the colour, which is one of the most beautiful and valuable, from an artistic point of view, in the whole range of metal colouring. Brass does not receive a light brown but a brownish to slaty drab, and with some solutions a dark neutral green. If, after swilling and drying out in sawdust, the coloured brass is heated to about 130° C., the surface film appears to fuse and form the beautiful light brown shade characteristic of coloured copper. If the heat be continued the colour disappears, and the brass is coated with a uniform deposit of copper. Also, if the brass article is removed from the source of heat as soon as the glaze appears, the light brown colour remains, and is but very slowly changed when exposed to daylight. In some cases no change occurs. If, however, the article be scratch-brushed a coating of copper is revealed.

[1] *Ding. pol. J.*, ccxxi. 38.

In this way brass may be as completely and uniformly coppered as by electro-deposition, but with this difference, that in the former case the coating of copper is exceedingly thin, while in the latter the thickness may be made to vary with the length of time it is exposed to the voltaic action. A brass article may be coppered by means of a solution of ferric chloride without any copper salt being present, but the result is not nearly so good. If, after bronzing a brass article in any of the before-mentioned solutions, it is scratch-brushed without heating, no coppering is seen, but simply a brass surface.

§ 74. Priwoznik makes the following observations concerning the action of various acids and salts on copper :—

When copper is immersed for a short time in a boiling solution of ammonium chloride, or in acetic acid, little or no action occurs, but after continued immersion a change occurs. When placed in a boiling solution of copper acetate it takes after a time a poor pale colour, but the solution is quite useless for effecting a good brown bronze suitable for such articles as medals. Hence neither of the above-mentioned liquids alone is suitable for bronzing. When ammonium chloride and copper acetate are mixed together a bluish-green deposit of hydrated copper oxychloride ($CuCl_2$, 3CuO, $4H_2O$) is produced.

Copper oxychloride cannot be used alone, but when ammonium acetate and acetic acid are added the oxychloride partly dissolves, and the solution formed may be used for bronzing copper. The insoluble residue should be filtered off and the clear solution only employed. It is better to dilute it with water and not to use it in the concentrated state.

For making a suitable bronzing solution with the last-

mentioned materials Priwoznik dissolves in 110 cubic centimetres (4 ounces) of vinegar about 17 grammes (260 grains) of precipitated copper oxychloride, by means of heat. As soon as the greater part of the excess of acetic acid is driven off, as shown by the crystalline deposit of green copper acetate on the surface, the solution is diluted with 4300 cubic centimetres (10 ounces) of water, then 12·7 grammes (190 grains) of ammonium chloride is added, and after a time the undissolved portion is filtered off. If the solution has not been boiled the filtrate will become muddy and prevent a uniform deposit. The liquid should contain about ·118 per cent of copper.

The colouring is effected chiefly by the formation of a film of cuprous oxide. This may be illustrated by the following experiments. Moisten a bronzed medal with a very dilute solution of sulphuric acid, and the moistened part will be blackened, because the cuprous oxide is changed to cupric oxide. If a portion of an alkaline solution of copper containing grape sugar is heated a precipitate of cuprous oxide is obtained. When this precipitate is collected, dried, and heated in a porcelain crucible, it becomes first brown, and then black, in consequence of its conversion to cupric oxide by means of the oxygen of the air. The same thing occurs when copper articles which have been bronzed with cuprous oxide are heated on an iron plate.

Reference has been made to the effect of light in producing changes in a bronze from a light to a darker tone. The most complete and most rapid change appears to occur on copper which has been bronzed in a copper chloride solution. From this it may be inferred that

metallic copper acts on cupric chloride, forming a thin film of cuprous chloride, as shown by the following equation :—

$$Cu + CuCl_2 = Cu_2Cl_2.$$

On exposure to light, even when the atmosphere has been excluded by a film of transparent lacquer, some change occurs which produces a dark coloured compound. It may be that the Cu_2Cl_2 is decomposed by the light into $CuCl_2$. By heating the copper which has been blackened by light to a temperature of 130° C. the original colour is restored.

Not only does copper undergo these actinic changes by the action of chlorine, but also its alloys, such as brass, though in a less degree. Some solutions containing chlorine impart to brass a beautiful greenish-yellow colour, which is but feebly susceptible to light, or only changes after a considerable time. The colour imparted will also depend on the composition of the metal. Pure copper will be coloured in a different manner to commercial copper, which may contain from 1 to 2 per cent of impurities, and the colour produced on brass will not only depend on the amount of copper present, but also on the impurities, *i.e.* on bodies other than copper and zinc, such as lead for example.

A vessel containing caustic potash or soda is generally kept boiling in a bronzing shop in order to remove grease from work before colouring. In time this becomes impregnated with metallic and other matters which have been dissolved or mechanically removed during the cleaning, and these foreign bodies, together with the potash itself, continue to discolour the work after the grease has been removed.

This coating is frequently iridescent, and becomes very firmly adherent to the metal, making it very difficult to be removed. In some cases this does not interfere with the subsequent colouring, but in others it does, in which case the work should have a previous dip in a solution of potassium cyanide. Also after articles have been dipped in aquafortis and then left for some time in the swill water a similar coloured and iridescent sheen will appear, but often darker than with potash.

An identical effect was produced as follows:—A box lid was dipped bright, rinsed in water, and placed on the top of a lacquering stove at the maximum temperature. The surface soon tarnished (became darker), then in a few minutes assumed a brassy hue, after which it became darker again, and iridescent brown and red films extended over the entire surface of the article, which was then removed from the stove and allowed to cool. A still longer exposure on the hot plate produced a dark reddish-brown, the relief parts remaining more or less bright.

By pickling in a strong boiling potash solution before heating upon the stove, the surface of an ordinary cast copper article was uniformly tarnished. When the same was heated in the manner described above, the entire surface became uniformly coloured. Another lid of cast copper which had been pickling in a solution of potassium permanganate for two days was uniformly tarnished, and on similarly heating on the stove assumed a darker reddish-brown colour. A brass figure pickled in aquafortis, swilled, and heated on the stove, did not assume any pleasing effect. A coppered cast-brass figure of a child heated on the stove for half an hour was covered

with iridescent green and crimson tints upon a brassy-brown ground. A coppered ash-tray simply became tarnished without showing any pleasing colour tints.

From these experiments it may be concluded that the effects in each case were due to the same cause, viz. oxidation of the metal by the combined means of the oxidising dip and the oxygen of the atmosphere.

§ 75. The following solutions are given to show the effect of chlorides or mixtures, in which a soluble chloride is one of the essential constituents:—

Cupric chloride	400 grains.
Water	4 ounces.

Dissolve the copper chloride in the water, raise to the boiling point and immerse the previously well cleaned copper articles for a few minutes. If the copper is pure, or nearly pure, a very beautiful rich reddish-brown colour will be obtained, but with ordinary commercial copper containing 1 to 2 per cent of impurities the colour obtained is nearly black.

On heating pure copper, after colouring in this solution, a fusion appears to occur upon the surface of the heated metal, which assumes a paler colour than before heating. These colours, with or without heating, blacken when exposed to daylight, although gaslight has no influence in changing the colour. It was thought at first that this action was due to oxidation by the air, but the same reaction occurred after a coloured article had been coated with transparent lacquer. The bluish-black colour produced by this actinic reaction is a very excellent colour, and we have used it very effectively in bronzing a certain part of an object which was required

to be black while the main portion was bronzed a lighter colour. This solution may therefore be very useful in such cases, or where an article is required to be finally coated with a bright black colour.

A number of experiments were performed in the author's laboratory to discover the cause of the above-mentioned change, and to find some means of arresting it so as to secure the most beautiful colour produced by copper chloride. We found that with copper bronzed in copper chloride the coating was a chloride, or a chloride mixed with some other compound of copper, for on treating the coloured body with ammonia till the coating was dissolved, and analysing the solution obtained, abundant evidence of chlorine was observed. Plates of copper were bronzed in this solution, and used for printing from photographic negatives. The pictures obtained were swilled with very dilute ammonia water so as to fix them, but they gradually faded.

A series of experiments were performed to ascertain whether the colour was due to a deposit superimposed on the copper, or due to corrosion of the surface of the article. It was found that the copper loses weight. The following results will show the amount of loss in each case :—

(*a*) Weight of coppered ash-tray	30·721
,, ,, ,, after bronzing .	30·587
Loss =	·134
(*b*) Weight of brass ash-tray	13·1413
,, ,, ,, after bronzing . .	12·8893
Loss =	·2520

(*c*) Weight of coppered ash-tray after bronzing .	30·587
,, ,, ,, after heating on stove	30·579
Loss =	·008
(*d*) Weight of brass ash-tray after bronzing . .	12·889
,, ,, ,, after heating on stove	12·899
Gain =	·010
(*e*) Weight of bronzed and heated brass ash-tray	12·8995
,, ,, after scratch-brushing	12·8700
Loss =	·0295
(*f*) Weight of bronzed and heated coppered ash-tray	30·5795
Weight of bronzed and heated coppered ash-tray after scratch-brushing . . .	30·5380
Loss =	·0415

Summary of the above results—

Copper	30·721
,, after bronzing	30·587
,, ,, heating	30·579
,, ,, scratch-brushing	30·538
Brass	13·1413
,, after bronzing	12·8895
,, ,, heating	12·899
,, ,, scratch-brushing	12·870

The following results were obtained with ash-trays bronzed in a solution of definite strength. One part by weight of copper chloride was dissolved in four parts of water :—

Coppered ash-tray	23·5115
,, after bronzing	23·4830
,, ,, heating	23·4800
,, ,, scratch-brushing . .	23·4445
Brass ash-tray	12·7445
,, after bronzing	12·5805
,, ,, heating	12·5840
,, ,, scratch-brushing . .	12·5470

§ 76. Similar colours to those produced on brass and copper by copper chloride may be obtained when ferric chloride is also added. The following were tried :—

Cupric chloride	30 grains.
Ferric chloride	30 ,,
Water	5 ounces.

The work required scratch-brushing and re-immersing to secure uniformity. Another solution was made with half the quantity of water, but with the same result as before. Another series of experiments was tried with a solution of

Cupric chloride	250 grains.
Ferric chloride	250 ,,
Water	10 ounces.

A coppered ash-tray received a reddish-brown colour as usual, and a casting of ordinary copper acquired a chestnut-brown. In this case the darker colour was doubtless due to the zinc, which is added to the copper in small quantity so as to produce sound castings.[1]

We have often observed with other solutions that while pure copper, such as is used for electrical work, receives a light brown colour, ordinary commercial copper turns

[1] See author's work on *Mixed Metals*, p. 75. Macmillan and Co.

almost black. The above solution was found to work best at a temperature of 50° to 60° C. It should be remembered that ferric chloride freely dissolves copper and brass when heated with them. Brass which has been bronzed in this solution has its coating decomposed by heat with the formation of a coating of copper, as in the case before mentioned, with copper chloride alone.

§ 77. Experiments were performed with a mixture of copper sulphate and ferric chloride. Although in this mixture no copper chloride is added at first, it is formed when the above salts are dissolved in water. The following proportions were employed :—

Copper sulphate (saturated solution), 16 ounces.
Ferric chloride (1 of salt to 4 of water), 1 ounce.

(*a*) Stamped brass tray, electro-coppered . .	light brown.
(*b*) ,, ,, ,, heated after pickling	lighter brown.
(*c*) Cast copper-plate	light brown.

In each case the surface blackened on exposure to daylight. If the work after being darkened by daylight is heated on a stove the black disappears, and the original colour, slightly altered in tone, is reproduced. This is again blackened on exposure to light, but the black colour has a blue tint as distinguished from the jet-black produced by the first exposure.

§ 78. The following solution was tried :—

Copper sulphate solution (1 of salt to 4 of water)	4 ounces.
Common salt	400 grains.
(*a*) Stamped ash-tray, electro-coppered .	brown colour, then white.
(*b*) Cast copper-plate	greenish-gray.

The brown colour of (*a*) turned white in the solution after a time, and after a day or two became green. The greenish-gray colour of (*b*) also turned to green in the same time. The above solution appears to be unsuitable for bronzing. If the metal after turning white is swilled and dried out in sawdust the colour is partly removed.

§ 79. Wuttig states that the usual antique bronze colour may be imparted to copper by a mixture of ammonium chloride, cream of tartar, common salt, and copper nitrate dissolved in water. He says "the pickle produces in a short time a very durable coating of oxide. The cream of tartar may be replaced by vinegar and the copper salt omitted after the copper has been once stained. With too much common salt the metal becomes yellower, with too little a bluish tint prevails." The following solution was employed by the author :—

Ammonium chloride	8 grains.
Cream of tartar (pure) . . .	24 ,,
Common salt	48 ,,
Copper nitrate	480 ,,
Water	5 fluid ounces.

(*a*) Electro-coppered brass ash-tray . . rich orange colour.
(*b*) ,, ,, ,, . . ,, ,,

(*a*) was simply pickled in the hot solution; (*b*) was pickled in the hot solution, swilled, dried out in sawdust, and heated on a hot plate, when it assumed a light nut-brown. The effects were the same as described under the head of copper chloride solution. Both blackened on exposure to daylight.

A similar solution to the above, but with the omission of the common salt, was tried, and although the same

effects were eventually obtained they took a much longer time to produce.

§ 80. The action of copper acetate in combination with a soluble chloride is said to give good results as a bronzing agent for copper. The following solution was tested :—

Copper acetate	180 grains.
Ammonium chloride . . .	60 ,,
Water	20 fluid ounces.

Some small brass ash-trays were electro-coppered and immersed in the hot solution. Those which had a thin coating of copper assumed a darker colour than those which had a strong coating.

(*a*) Ash-tray well coppered . . .	light red ochre colour.
(*b*) ,, with thin coating of copper	brown, darker than (*a*).
(*c*) ,, ,, ,,	,, ,,
(*d*) Brass ash-tray	yellowish-brown.

The tray marked (*c*) was coppered by pickling in copper chloride solution and then heating on the stove, by which method the coating is always exceedingly thin but perfectly uniform. All these colours became darker on exposure to daylight.

§ 81. Copper acetate and ammonium chloride dissolved in vinegar and water, and containing red iron oxide in suspension, has been recommended for bronzing. The following proportions were tried :—

Copper acetate	180 grains.
Iron oxide	180 ,,
Ammonium chloride	60 ,,
Vinegar	4 fluid ounces.
Water	16 ,,

(*a*) Coppered ash-tray . . .	bright light brown.
(*b*) ,, ,, ...	light red ochre.

(*b*) was pickled in the hot solution, dried out in sawdust, and heated on the lacquering stove, when it assumed the above-mentioned colour; (*a*) was simply pickled, swilled, and dried out.

The following solution was also tried :—

Copper acetate	180 grains.
Iron oxide	180 ,,
Ammonium chloride . . .	60 ,,
Water	20 fluid ounces.

The results were much the same as in the former solution, but the colours were darker and with a less brilliant lustre. The bronzed trays were exposed to full daylight during a clear February morning. One tray, which was simply pickled, darkened a little; another, which was heated after pickling, appeared to be unchanged. They would both gradually blacken if exposed to the direct rays of the sun in summer.

§ 82. A solution composed of copper sulphate and copper chloride and water gave the following results :—

Copper sulphate	400 grains.
,, chloride	400 ,,
Water	4 fluid ounces.
(*a*) Electro-deposited copper . .	light orange.
(*b*) High conductivity copper . .	,,
(*c*) Commercial copper	brownish-black.

The metals were pickled in the hot solution, swilled, and dried out in sawdust, when they had the above appearance. They all became black after exposure to daylight. On

repeating the experiments, but with a subsequent heating after pickling, the colours were darker, but the surfaces not uniform.

§ 83. Coppered ash-trays were immersed in a hot solution composed of the following ingredients :—

Copper chloride and ammonium chloride ($CuCl_2$, 2AmCl) . . .	500 grains.
Water	5 ounces.

The trays assumed a beautiful reddish-brown colour, which soon turned to black on exposure to daylight. On strongly heating the trays, after bronzing, until the surface blackens, and then allowing to cool, a fine purplish-red colour appears, but the coating rubs off easily and exposes a copper surface. By coating the surface with transparent lacquer (zapon) without previously touching, the red colour becomes fixed, but does not appear so dense after the lacquering process as before.

A series of experiments with this solution showed that it works better cold than when hot. A freshly prepared solution imparts a richer colour to electro-deposited copper than it does after some time of working.

§ 84. The following complex mixture is given by Haldane for bronzing copper. The proportions given below were tried—

Copper acetate	5 grains.
,, sulphate	20 ,,
Common salt	7 ,,
Sulphur	14 ,,
Acetic acid	10 cubic centimetres.
Water	5 fluid ounces.

A coppered ash-tray immersed in the hot solution received a terra-cotta colour, which afterwards became nearly black on exposure to daylight. A plate of commercial copper acquired a steely-copper bronze.

During the working of this solution a black precipitate of copper sulphide separates out, causing the solution to become paler in colour. This precipitate clings to the edges of the work and blackens it, but not very much. No advantage was obtained by heating the work previous to immersion.

§ 85. A solution, consisting of copper chloride and tartaric acid dissolved in water, and sodium hydrate added, has been recommended for bronzing. The following proportions were used, with the results given below :—

Copper chloride solution .	1 fluid ounce (1 of salt to 4 of water).
Tartaric acid . . .	75 grains dissolved in water.
Sodium hydrate solution .	1¼ fluid ounces (1 of alkali to 5 of water).
(*a*) Coppered ash-tray . .	yellowish-brown colour.
(*b*) A copper electrotype . .	,, ,,

Both darkened on exposure to daylight. A brass tray immersed in the hot solution first assumed a golden yellow, then deep gold, nut-brown, and yellowish-brown. If immersed longer the ordinary brass colour reappears.

§ 86. According to Böttger, copper can be bronzed a yellowish-brown colour by immersion in a solution of ammonium nitrate and potassium chloride. By heating the bronzed article after swilling and drying, it assumes a dark reddish-brown colour.

A saturated solution of the above salts in equal proportions was tried by the author and used boiling. Copper articles were boiled in the solution, even until the salts began to crystallise upon them, without any perceptible change occurring on the copper. The work was also immersed in the solution, and dried upon the hot stove without previous rinsing, but no useful effect was produced. The work was then rubbed with the concentrated solution by means of a cloth, without any noticeable change of colour. The solution appears to be quite worthless as a bronzing agent either for copper or brass.

§ 87. Kayser recommends the following solution :—

Ammonia	20 grammes.
Acetic acid in slight excess of the ammonia.	
Ammonium chloride . . .	10 ,,
Water	1 litre.

By painting this solution on to the work, allowing it to dry, and then rubbing, the copper assumes a brown tone. The operation must be repeated several times.

This solution was tested in the following ways :—

The work was pickled during a long time in the hot solution, dried gently on the hot stove, and then rubbed. The operation was repeated several times, according to Kayser's instructions, without any useful effect. After a considerable time of working the solution became green from the presence of dissolved copper, and then acted slightly on the work.

§ 88. The following solution has been recommended for bronzing copper, but we found it to be practically useless both for copper and brass :—

Ammonium chloride	356 grains.
Oxalic acid	89 ,,
Acetic acid (6 per cent solution) .	30 fluid grains.
Water	6 fluid ounces.

No action was perceived on copper after a long continued immersion in the hot solution. Rubbing the solution on to the copper simply gave it a dull stain. Pickling the work in the solution and drying on stove without rinsing gave no useful result. The copper received a very poor terra-cotta colour, which was darkened by daylight.

§ 89. A dark brown colour on copper is said to be obtained by immersing the articles in the mixtures enumerated below—

(1)	Copper nitrate	1 ounce.
	Hydrochloric acid	5 ounces.
(2)	Copper nitrate	½ ounce.
	,, chloride	½ ,,
	Hydrochloric acid	5 ounces.

The work is recommended to be pickled in the solution (1) and then immersed in the solution (2). The following are the results obtained by the author with these liquids :—

(*a*)	Coppered ash-tray immersed in the solutions		purplish-pink.
(*b*)	,,	,, (*a*) cold, (*b*) hot	,,
(*c*)	,,	,, (*a*) hot, (*b*) cold	,,
(*d*)	,,	,, both solutions used hot	,,

These solutions are of no permanent use, as the colour produced on copper is blackened by exposure to daylight. The hot solution dissolves both brass and copper rapidly. The bronzing effect on brass is practically *nil*.

§ 90. Buchner recommends the following solutions for bronzing electro-deposited copper :—

I.	Copper nitrate,	neutral	solution	containing	100	salt	900	water.
II.	,,	,,	,,	,,	200	,,	800	,,
III.	Calcium chloride	,,	,,	,,	100	,,	900	,,
IV.	,,	,,	,,	,,	200	,,	800	,,
V.	Mercury chloride	,,	,,	,,	50	,,	950	,,
VI.	Tin chloride	,,	,,	,,	100	,,	900	,,

Mix equal parts of I. or II. with III. or IV. according as a darker or lighter shade of colour is required. That good colours may be obtained by the above recipes is shown by the results of the preceding experiments with similar solutions in which a soluble chloride is present, but they suffer from the same great defect, viz. the alterability on exposure to light, causing them to assume very dark and irregular shades of colour.

§ 91. The various solutions which have been described in the preceding pages owe their virtue chiefly to the formation of a chemical compound, such as an oxide, a chloride, etc., and the deposition, or rather formation of the same on the surface of the copper immersed in it.

It has also been proved that in every case where a chloride was employed that the colour deepened considerably in tone by exposure to daylight, which greatly limits the usefulness of such solutions. There is one chloride, however, which is not subject to variation by the action of light, but the shade is blackish, and altogether different to the beautiful light browns produced by certain other soluble chlorides. This difference is due to the deposition of a thin film of metal on the copper instead of a metallic compound. The following results have been obtained by the use of platinum chloride solutions :—

Thoroughly clean the work in the usual way, and then immerse it in a solution of

Platinum chloride	1 grain.
Water	500 grains.

When the article has become tarnished all over then transfer it to a stronger solution containing

Platinum chloride	$2\frac{1}{2}$ grains.
Water	500 ,,

Allow the work to remain in the solution until the requisite depth of colour has been attained. Buchner recommends to previously cleanse the work by pickling it in a solution of cream of tartar, but this does not appear to be of any advantage if the articles are properly cleaned in the usual way.

(*a*) Coppered ash-tray, after scratch-brushing .	light steel-gray, with a reddish tint.
(*b*) ,, ,, ,, .	light steel-gray, with a reddish tint, but more opaque.
(*c*) ,, but with longer immersion .	nearly black.
(*d*) Brass tray ,, ,, .	lighter than (*c*).

The tray (*a*) was done in the weaker solution only, and scratch-brushed. The tray (*b*) was done in both solutions as directed above. The colouring in each case is due to the deposition of a thin dark film of metallic platinum. The stronger solution gives a more dense deposit than the first one, and scratch-brushing in each case renders the colour paler.

Moreover, as the above is a case of deposition of platinum by simple immersion, one would not expect the colour on brass to differ much from that produced on copper, and that such is the fact is proved by the result of experiment (*d*). Any difference observed must be due to the coating of platinum being so thin as to be semi-transparent, and allow the underlying metal to be seen somewhat through it; this is notably the case with

the platinised copper tray (*a*), which was well scratch-brushed after immersion in the bronzing solution.

Leaving the work too long in the solution is wasteful, as, beyond a certain limit, all the platinum deposited is in pulverulent state, and easily rubs off, either in drying out in sawdust, or under the action of the scratch-brush. Heating the work after bronzing in a platinum solution does not appear to improve it, and if the article is made too hot the uniformity of the colour is destroyed.

The following proportions were also tried with the results recorded below :—

Platinum chloride	1 part.
Water	5 parts.

Copper and brass work were painted with this solution with the production of a dark gray deposit. On evaporating the solution to dryness and redissolving the residue in alcohol the following results were obtained :—

(*a*) Brass tray . .	black at front, platinated at back.
(*b*) Coppered tray .	black.

The tray (*a*) was scratch-brushed at back only ; the tray (*b*) was not scratch-brushed. It appears from these experiments that if a black colour is desired the platinum chloride should be dissolved in alcohol. The deposit is more firmly adherent to brass than to copper.

§ 92. The following solutions, although containing ammonium chloride, are chiefly effective on account of the sulphur compound with which it is associated. The colours obtained are darker than with chlorides alone, since the sulphides tend to produce copper sulphide, which is black, but the presence of the chloride modifies the dark tone, producing a compound colour of a reddish tint.

Potassium sulphide	30 grains.
Ammonium chloride . . .	90 ,,
Water	5 fluid ounces.

If the work to be coloured is large and unsuitable for the immersion process then the solution may be applied with a sponge, and the work allowed to stand exposed to the air from half an hour to an hour until dry, and then scratch-brushed. The operation will require to be repeated one or more times to get a satisfactory shade of colour. When this is secured, finish by brushing with a waxed brush. The following results were obtained from experiments with the above solution :—

(*a*) Coppered ash-tray . .	reddish-brown colour.
(*b*) ,, ,, . .	rich purplish-brown.
(*c*) ,, ,, . .	,, purplish-gray.
(*d*) ,, ,, . .	,, light purplish-red.

The tray (*a*) was done as described above by sponging on the solution ; (*b*), (*c*), and (*d*) were immersed for varying lengths of time in the solution and became coloured much more rapidly, especially with a hot solution. This solution is not suitable for brass in consequence of the great length of time required to produce a useful colour, which varies from a coppery-red to brown. The solution acts very vigorously on copper, the colour passing from light crimson through various shades of purple, red, purplish-gray to plumbago-black. If the bronzing has produced too dark a shade of colour, it may be made lighter by scratch-brushing.

This solution soon becomes exhausted, as after about half an hour's working its action is very slow, even upon copper. The effectiveness of the above mixture is doubtless due to the formation of ammonium sulphide, which

produces copper sulphide upon the metal. When the liquid is freshly prepared and warm, the well-known odour of sulphuretted hydrogen is perceived, but when it begins to work somewhat tardily, the odour perceived is more like water in which flowers of sulphur is suspended.

Another solution and stronger than the former was tried, using the following proportions :—

Potassium sulphide . . .	150 grains.
Ammonium chloride . . .	2000 ,,
Water	5 fluid ounces.

The work was immersed in the solution—

(*a*)	Coppered ash-tray	light purple-red.
(*b*)	,, ,, ...	darker ,,
(*c*)	,, ,, ...	bluish-black.
(*d*)	,, ,, ...	plumbago-black.
(*e*)	,, ,, ...	jet-black.

It will be observed that this solution only differs from the preceding one in density, containing five times as much salt dissolved in the same amount of water.

(*a*), (*b*), and (*c*) were all done in the warm solution, and each one was patchy in appearance when removed, but became uniform and lighter in colour on scratch-brushing; (*d*) and (*e*) were done in the cold solution; (*d*) was simply dried out in sawdust and brushed with a soft brush; (*e*) was simply rinsed in alcohol and then coated with the transparent lacquer termed "zapon."

§ 93. Copper nitrate forms a very useful medium for bronzing copper articles, in consequence of its oxidising nature, varying with the strength of the solutions employed.

When the amount of copper nitrate is small, and the quantity of water very large, then merely a stain is produced by the immersion of brass or copper in it; but with stronger solutions electro-deposited copper is coloured a beautiful light chestnut-brown.

A very slight amount of impurity present in the copper is sufficient to alter the tone of colour. A solution, just sufficiently strong to effect the change on copper mentioned above, will turn an article of ordinary commercial copper dark brown, almost black. Even with samples of commercial copper of approximate purity the colour is not perfectly uniform all over the surface, and is generally iridescent, instead of a good solid colour, such as is obtained on pure copper.

A solution of the following strength is recommended :—

Copper nitrate	800 grains.
Water	6 ounces.

High conductivity copper received a purplish-chocolate colour when immersed in the hot solution; commercial copper assumed a blackish stain; and brass a dark sage-green. On heating after immersion the work became irregular in colour and patchy in appearance.

A saturated solution of copper nitrate was next tried, with the following results :—

(*a*) A coppered ash-tray, heated on the lacquering stove, and immersed in the solution assumed a chestnut-brown.

(*b*) A coppered tray, immersed without previous heating, received a chocolate, inclining to purple colour.

(*c*) A cast copper-plate, heated and plunged into the solution, turned to an Indian red colour on the high relief parts, and umber-brown on the groundwork.

A black may be obtained with this solution, both upon brass and copper, by immersing the articles in the solution and transferring them to the hot stove without rinsing. If the work is covered with an inverted glass beaker, it will be observed to dry of a light green colour, with the production of brown fumes. After a little time, the green colour changes to a dead black, which, on brushing with a soft brush, assumes a uniform and bright appearance.

§ 94. A copper nitrate solution containing 15 per cent of the salt, to which sufficient potash was added to produce a slight precipitate, gave the following results :—

(*a*) Coppered ash-tray . . .	shellac-brown.
(*b*) Commercial sheet-copper . .	,, but paler, with iridescent patches.

Similar solutions to the above, but containing 10 and 20 per cent of salt respectively, gave similar results. Ordinary sheet-copper appears to change more rapidly in each of the three solutions than electro-deposited copper, but the colour is not nearly so rich in tone. Electro-deposited copper, after bronzing in copper nitrate, will withstand a much more vigorous scratch-brushing without exposing the bare metal than ordinary copper under similar treatment.

§ 95. The following solution yields very good results, both for copper and brass :—

Copper nitrate, 20 per cent solution .	3 fluid ounces.
,, acetate, saturated solution .	3 ,,

A brass tray by immersion assumed a neutral greenish-brown ; a coppered tray received a light-coloured bronze of a very pleasing appearance ; a piece of ordinary sheet-copper became reddish-brown with iridescence.

The following solution acts very similar to the preceding one, but yields a deeper tone of colour with more of a reddish hue, and inclining to iridescence :—

Copper nitrate, 20 per cent solution .	3 fluid ounces.
,, acetate, saturated solution . .	6 ,,

The following proportions were also tried :—

Copper nitrate, 20 per cent solution .	1 fluid ounce.
,, acetate, saturated solution . .	4 fluid ounces.
(*a*) Coppered tray	reddish-brown.
(*b*) Ordinary sheet-copper . . .	,, but with iridescence.

It should be noted that with all solutions containing acetic acid, or an acetate, there is more or less iridescence, which in many cases is objectionable on account of the lack of uniformity it imparts to a plain surface, which is generally required to be of the same shade throughout. This effect is most marked in ordinary copper, in consequence of the impurities it contains. With all solutions containing copper nitrate as a principal ingredient, the work may be rendered paler in colour by scratch-brushing.

§ 96. Copper nitrate gives an acid reaction which has a solvent action on copper and brass, and therefore it is thought desirable in some cases to neutralise it with ammonia. When ammonia is added to a soluble copper salt it first precipitates the hydrated oxide, but on the addition of more ammonia the precipitate is redissolved. This solution gave the following results :—

Copper nitrate	400 grains.
Water	1 pint.

Ammonia in sufficient quantity to just redissolve the precipitate at first formed.

A coppered ash-tray pickled in the cold solution assumed a dirty chocolate-drab colour. On swilling and drying out in sawdust the drab colour disappeared, and the surface presented a coppery hue. The result was probably due to excess of ammonia, which dissolves many copper deposits as well as copper itself. On heating after pickling, and then re-immersing when cold in the same solution made hot, a smoky chocolate colour streaked with black was produced. A brass tray pickled in the above solution became dark brown; and when pickled in the hot solution received a still darker shade of colour. Excess of ammonia may be removed by boiling the solution for some time. There appears to be no advantage gained by adding ammonia to copper nitrate, except in very small quantity.

§ 97. The addition of tartaric acid to copper nitrate and sodium hydrate is said to produce a good bronzing mixture. The following proportions were tried :—

Copper nitrate	1 ounce.
Tartaric acid	200 grains.
Sodium hydrate	250 ,,
Water	8 fluid ounces.

Very little effect was produced on brass or copper. The tartaric acid seems to prevent or to considerably retard the action generated by the solution in § 94. Four drachms of ammonia were then added to the above solution, which caused the liquid to work much more satisfactorily and imparted to a coppered ash-tray a good permanent nut-brown colour.

With respect to black bronzes the *Zeitschrift für Instrumentenkunde* (X. Jahrg., Mai 1890), says—

"The best result is obtained by the following mixture: 600 grammes of copper nitrate is dissolved in 200 c.c.

of distilled water, and to this solution is added 2·5 grammes of silver nitrate which has been dissolved in 10 c.c. of distilled water.

"The addition of the silver nitrate to the solution greatly assists in the formation of the proper colour. More than the above-mentioned quantity, however, is not advisable. If the solution is too concentrated, some of the salt will crystallise out, and more distilled water should be added to redissolve it. The articles to be bronzed must be perfectly clean, and especially be free from grease. They may be cleansed by dipping in a mixture of 1 part common hydrochloric acid and 1 part water, or a mixture of 2 parts concentrated sulphuric acid and 7 parts water. In such dilute acids the articles may be suspended by means of brass wire for five or ten minutes, then well swilled with water and immersed in the hot bronzing bath. If the article is too large for immersion, it may have the solution painted on by means of a brush. A thin painting of the solution is not recommended, as it is apt to make the colour patchy. After the work is taken out of the solution, any collection of liquid in any one place must be avoided, and the metal is then left to slowly dry. Too quick drying is likely to produce spots. In a short time a pale green deposit appears on the surface. If the process has gone on satisfactorily the metal can now be put into a hot flame, when the green colour changes to black. After cooling, the surface is brushed with a not too hard brush.

"The above method is very useful for copper, brass, gilding metal, German silver, and the various bronzes. The method gives a beautiful bronze, but it is likely to be not quite uniform."

LIGHT TO DARK BROWN COLOURS ON COPPER

§ 98. Copper sulphate is a most useful bronzing reagent, and is capable of producing some very beautiful effects. The following proportions have been tried by the author :—

Commercial copper sulphate . .	400 grains.
Water	2 ounces.

The solution is best used warm, and after two or three immersions with scratch-brushing, if necessary, a uniform light brown colour is obtained on pure copper, and a much darker shade on ordinary copper.

(*a*) Electro-deposited copper . .	terra-cotta brown.
(*b*) High conductivity ,, . .	purplish-chocolate.
(*c*) Commercial copper . . .	dark brown.

The dark brown colour on commercial copper becomes almost black if the metal contains much impurity.

§ 99. Experiments were next performed with copper sulphate and ammonia.

Copper sulphate (com.) . . .	200 grains.
Water	5 ounces.
Ammonia in sufficient amount to precipitate and redissolve copper hydrate.	

(*a*) High conductivity copper . .	light brown.
(*b*) Ordinary copper	purplish-brown.
(*c*) Brass	yellowish-brown.

It should be remembered that ammonia in excess dis-

solves copper, so that any excess should be removed by boiling the solution.

§ 100. The following solution produces good results, but the action is slow. It works much better after boiling for some time, from which it may be inferred that a stronger solution is preferable :—

Copper acetate	300 grains.
,, sulphate	200 ,,
Water	2½ pints.

(*a*) High conductivity copper	brownish pale terra-cotta.
(*b*) Ordinary copper . .	dark purple by long immersion.
(*c*) Brass	copper-coloured bronze.

§ 101. The following experiments were undertaken with a view to ascertain the cause of the colouring effect, whether it is due to a deposition of a copper compound on the metal, or whether the change is due to a corrosion of the surface, and consequent loss of metal. A solution was used consisting of

Copper sulphate (com.) . . .	4 ounces.
Water	8 ,,

(*a*) Brass ash-tray	pale umber-brown.
(*b*) Coppered ash-tray	brownish terra-cotta.
(*c*) Cast brass-plate	light reddish-brown.
(*d*) Cast copper-plate (com.) . .	chestnut-brown.
(*e*) Coppered ash-tray, strongly coated	nut-brown.

Some of the above brass and copper articles were weighed before and after bronzing, with the following results :—

	Brass.	Copper.
Before bronzing . .	206·9 grains.	452·15 grains.
After ,, . .	206·5 ,,	455·10 ,,
	Loss = ·4 grains.	Gain = 2·95 grains.

	Brass.	Copper.
Before bronzing . .	184·20 grains.	497·55 grains.
After ,, . .	184·07 ,,	497·25 ,,
	Loss = ·13 grains.	Loss = ·30 grains.

The above experiments would tend to show that copper receives a deposit at the expense of the solution, although in the second trial the copper lost weight. Copper bronzes somewhat slowly in a copper sulphate solution, while brass bronzes rapidly, especially if after once pickling in the solution it is swilled and scratch-brushed, then re-immersed.

If brass is heated on a stove after bronzing it loses its umber-brown colour and assumes the appearance of a very pale coinage bronze. When the bronzed copper article is similarly treated it slightly darkens in tone, but if strongly heated it passes through a purplish-chocolate colour to black by the formation of black copper oxide, which readily peels off and exposes the copper. It will be seen from these experiments that the impurities present in commercial copper exert an influence in modifying the tone of colour.

§ 102. Another solution containing copper sulphate was found to yield excellent results. The proportions employed for the experiments were—

Copper sulphate	580 grains.
Water	45 fluid ounces.

Boil till the copper salt is dissolved, neutralise with sodium hydrate, then add 770 grains of red iron oxide. Immerse the work in the solution for a short time, and heat to below redness. Well swill in water and repeat

the operation till a satisfactory brownish-red colour is obtained.

(*a*) Coppered ash-tray . .	reddish to dark brown.
(*b*) Ordinary cast copper . .	lighter brown.
(*c*) Electrotype copper . .	rich reddish-brown.
(*d*) Coppered ash-tray . .	similar to (*a*) but lighter.
(*f*) ,, ,, . .	similar to (*a*).

(*d*) was obtained by immersion only, which accounts for the lighter tone of colour. By heating, as in the case of (*a*), (*c*), and (*f*), a darker shade is produced. The process may have to be repeated several times to get the desired depth of colour. The colour is much richer and denser with pure than with impure copper. The best method of heating is by means of a charcoal fire. The colour is modified by the length of immersion and by the temperature.

§ 103. The solution referred to in this paragraph may be useful for some varieties of copper goods, as the general shade of colour is pleasing in tone, but it is unsuitable for plain surfaces, in consequence of the iridescence which accompanies all bronzing in liquids containing acetic acid, or a soluble acetate.

Copper sulphate	15 grains.
,, acetate	25 ,,
Water	8 fluid ounces.
Alum	10 grains.

(*a*) Coppered ash-tray .	shellac-brown, with bluish sheen.
(*b*) ,, ,, .	,, ,,

The above results were obtained by heating on a hot iron plate after immersion, swilling in water, and drying out in sawdust. The colours are permanent.

§ 104. The following solutions containing copper sulphate

have been recommended for bronzing, but no useful results were obtained from them by the author's experiments. They also react on copper and brass very slowly with regard to colouring :—

I.
- Copper sulphate . . . . . 1000 grains.
- Water . . . . . 10 fluid ounces.
- Then add solution of caustic potash containing 1500 grains dissolved in 15 fluid ounces of water. Also oxalic acid 200 grains.

II.
- Copper sulphate . . . . . 250 grains.
- Cream of tartar . . . . . 125 ,,
- Water . . . . . 5 fluid ounces.
- Then add to the above a solution of caustic potash containing 125 grains dissolved in 5 fluid ounces of water.

III.
- Copper sulphate . . . . . 240 grains.
- Water . . . . . 2 fluid ounces.
- Tartaric acid . . . . . 150 grains, dissolved in 1½ ounces of water.
- Sodium hydrate . . . . . 192 grains, dissolved in 2 fluid ounces of water.

A brass tray immersed in No. III. solution only assumes a brownish-yellow colour, and a coppered tray a brassy yellow, after leaving in the solution for two days. The same trays were then kept immersed in a boiling solution until the latter was so concentrated that it solidified on cooling.

A fresh solution of the composition No. III. was made, and a slight excess of ammonia added. It gave the following results after the articles had been immersed a considerable time :—

(*a*) Coppered ash-tray . . .	pale shellac-brown.
(*b*) Brass ash-tray . . .	pale greenish-brown.
(*c*) Brass casting	light brown.
(*d*) Copper casting . . .	,,

The results were uncertain and could not be exactly reproduced.

§ 105. **Japanese Bronze.**[1] — According to Roberts-Austen, the Japanese employ a wide range of alloys, many of which contain silver and gold in varying proportions. The following are examples :—

SHAKU-DO

I.		II.	
Copper . .	94·50	Copper . .	95·77
Silver . .	1·55	Silver . .	·08
Gold . . .	3·73	Gold . . .	4·16
Lead . . .	·11		
Iron and arsenic	traces		
	99·89		100·01

The quantity of gold is very variable, and certain specimens examined by the above authority contained only 1·5 per cent of gold. The next important alloy used by the Japanese is called "Shibu-ichi," of which the following are typical analyses :—

SHIBU-ICHI

III.		IV.	
Copper . .	67·31	Copper . .	51·10
Silver . .	32·07	Silver . .	48·93
Gold . . .	traces	Gold . . .	·12
Iron . . .	·52		
	99·90		100·15

There are many varieties of it, but in both these alloys,

[1] *Jour. Soc. of Arts*, 26th Oct. 1888.

"Shaku-do" and "Shibu-ichi," the point of interest is that the precious metals are, as it were, sacrificed in order to produce definite results, gold and silver, when used pure, being employed very sparingly to heighten the general effect. In the case of "Shaku-do" the gold appears to enable the metal to receive a beautiful rich purple coat or patina when treated with certain pickling solutions, while "Shibu-ichi" possesses a silver-gray tint of its own, which, under ordinary atmospheric influences, becomes very beautiful, and to which the Japanese artists are very partial.

These are the principal alloys, but there are several varieties of them, as well as combinations of "Shaku-do" and "Shibu-ichi" in various proportions, as, for instance, in the case of "Kiu-shibu-ichi," the composition of which would correspond to one part of "Shaku-do" rich in gold, and two parts of "Shibu-ichi" rich in silver.

With regard to pickling solutions Roberts-Austen states that the following are largely used :—

	I.	II.	III.
Verdigris	438 grains	87 grains	220 grains.
Copper sulphate	292 „	437 „	540 „
Nitre	...	87 „	...
Common salt	...	146 „	...
Sulphur	...	233 „	...
Water	1 gallon	...	1 gallon.
Vinegar	...	1 gallon	5 fluid drachms.

That most widely employed is No. I. When boiled in No. III. solution, copper will turn a brownish-red, a "Shaku-do" becomes purple. Copper containing a small quantity of antimony gives a shade very different from that resulting from the pickling of pure copper. It is

strictly accurate to say that each particular shade of colour is the result of minute quantities of metallic impurity. The action of these solutions then produces entirely different effects on pure copper to that produced on the impure metal.

The following experiments were performed by the author, using No. I. solution worked hot:—

(*a*) Coppered ash-tray . . light brown.
(*b*) Brass ash-tray . . . umber-brown, with bluish sheen.
(*c*) Copper casting (com.) . ,, ,, ,,

On the high relief parts the colour was umber-brown, with a bluish sheen, and a tendency to iridescence, while on the groundwork the colour was umber-brown, with a tendency towards blue.

(*d*) Brass casting . . . coppery umber-brown.

Electro-deposited copper bronzed very slowly and cast copper less slowly. Commercial sheet-copper, containing 99 per cent copper and 1 per cent arsenic, and other impurities, bronzed quickly, and the same with sheet-brass, but cast-brass was only slowly affected. In all the above cases the articles required to be scratch-brushed and the operation repeated to secure uniformity. The solution after a little working yields a pale green precipitate and a nearly colourless liquid. The colours obtained are permanent in the light.

No. I. solution was again tried, but with placing a piece of zinc in contact with the work.

(*a*) Coppered ash-tray — umber-brown, with incipient blue sheen.
(*b*) Ordinary cast-copper — umber-brown, but darker than (*a*).
(*c*) Brass casting . — pale umber-brown on the high relief parts, and coppery-brown on the groundwork.

Contact with zinc appears to hasten the process on first immersion. I have observed that the first change produced on the work in the bronzing solution is, in many cases, a tarnishing of its surface (oxidation?).

If, after this tarnishing has occurred, the work is rinsed in water, scratch-brushed, and re-immersed in the solution, the tarnishing goes on much more rapidly and more uniformly than on first immersion, and this second tarnishing is quickly followed by the colour proper to the solution and metal concerned in the process. There is a tendency to the production of iridescent colours, especially on cast-copper work pickled in this solution, and it is possible to arrest the process at the moment these colours appear. If the work is lacquered the colours are permanent, not being altered by exposure to daylight, except that the blue sheen largely disappears.

§ 106. The following solution yielded results as recorded below, using a mixture of :—

Copper acetate	11 grains.
,, sulphate	54½ ,,
Common salt	18 ,,
Nitre	11 ,,
Water	1 pint.

(*a*) Coppered ash-tray	light brown.
(*b*) ,, ,,	lighter brown than (*a*).
(*c*) ,, ,,	redder ,,
(*d*) Cast-copper	drab-brown.

(*a*) was immersed in the hot solution, swilled, scratch-brushed, and re-pickled; (*b*) was pickled, then heated on hot plate, and the immersion repeated; (*c*) was pickled, heated over a Bunsen burner, and again re-immersed in the solution; (*d*) was pickled, scratch-brushed, and re-pickled.

On exposure to daylight (*a*) became black, (*b*) and (*c*) darkened and showed a tendency to blacken, (*d*) became nearly black.

§ 107. The following mixture, which is the same as the preceding one, with the omission of the common salt, was then tried :—

Copper acetate	11 grains.
,, sulphate	54½ ,,
Nitre	11 ,,
Water	1 pint.

(*a*) Coppered ash-tray	pale umber-brown, with yellowish sheen.
(*b*) Cast-copper	reddish-umber-brown.
(*c*) Brass	purplish stain.

These colours remain permanent on exposure to daylight, so that the solution is much more suitable as a bronzing agent than the preceding one, which contains a soluble chloride, and therefore produces a film which blackens on exposure to daylight.

§ 108. Instead of using the recipe given in the last section, similar results of a permanent character may be obtained from the following solution :—

Copper acetate	28 grains.
,, sulphate	135 ,,
Vinegar	40 fluid grains.
Water	20 ounces.

The vinegar employed should be of good quality and free from sulphuric acid, otherwise it is preferable to use a 6 per cent solution of acetic acid in place of the vinegar. The following results were obtained :—

(*a*) Coppered ash-tray	light umber-brown.
(*b*) Cast-copper ornamental plate . .	yellow umber on the groundwork, and yellowish sheen on the relief parts.
(*c*) Coppered ash-tray	dull red.

(*a*) and (*b*) were immersed in the hot solution for some time, then swilled and scratch-brushed. The operation was again repeated, and the metals dried out in sawdust without a previous scratch-brushing; (*c*) was bronzed, swilled, and dried out in sawdust, then heated on a hot plate until it assumed a dull red colour, when it was scratch-brushed to produce uniformity, re-immersed, swilled, dried out in sawdust, and brushed with soft brush to finish, when it appeared as a chestnut-brown.

DARK BROWN TO BLACK COLOURS ON COPPER

§ 109. A dilute solution of ammonium sulphide used cold yields very beautiful effects; as shown by the following results:—

(*a*) Coppered ash-tray . . .	light nut-brown.
(*b*) ,, ,, . . .	,, but darker.
(*c*) ,, ,, . . .	dark brown.
(*d*) ,, ,, . . .	steely brown.
(*e*) ,, ,, . . .	grayish-black.
(*f*) ,, ,, . . .	dead black.

This solution works very well for copper, but it is not suitable for brass. If, however, brass work is thinly coated with copper, then this method will produce the colours enumerated above. The solution works well

either hot or cold, strong or dilute. The colours depend more upon the manipulation of the process than upon either temperature or density. Colours may be obtained, ranging from a neutral crimson through brown and steel-gray to black.

(*a*), (*b*), (*c*), and (*d*) were all scratch-brushed, the lighter colour on (*a*) was obtained by a momentary immersion only, which produces such a transparent film that the copper can be seen through it, modified, of course, in tone by the thin coating of copper sulphide; (*e*) was dried out in sawdust without scratch-brushing; (*f*) was rinsed in alcohol after immersion in the bronzing solution, and the alcohol burnt off, leaving a black velvety coating, which is fixed on the metal by dipping it in zapon. As long as the film is sufficiently thin a reddish-brown tint is visible, but when a certain thickness prevails the colour is black without any trace of red.

This solution may be used for bronzing work which is too large to immerse in the solution, by moistening it with a sponge or cloth, then allowing the articles to stand exposed to the air till they are dry, when they may be scratch-brushed, and the moistening repeated if the colour is not deep enough, or the bronzing not uniformly distributed. When the right tint is attained, the articles should be thoroughly washed, first with warm water, then with cold water, and finally dried out in sawdust and brushed with a waxed brush.

§ 110. A similar solution may be formed by dissolving potassium sulphide (liver of sulphur) in water. The following were tried :—

I.	Potassium sulphide	½ part.
	Water	99½ parts.

A coppered ash-tray assumed a dark steel-gray colour after immersion in the solution

II.	Potassium sulphide	$\frac{1}{4}$ part.
	Water	$99\frac{3}{4}$ parts.

A coppered ash-tray received a reddish-gray colour. The remarks made with regard to the ammonium sulphide solution apply also to potassium sulphide. The colour may be modified in the manipulation of the working of both solutions. Darker colours can be produced by a longer immersion, and these again can be further modified by judicious scratch-brushing.

§ 111. The following solution has been recommended for producing a reddish-brown colour, which becomes paler on heating :—

Dissolve 1 part of copper acetate in 16 parts of water, then add sufficient ammonia to give a deep blue solution, and add 2 parts of potassium sulphide, 3 parts of ammonia, and 10 parts of water. The following was used by the author :—

Copper acetate	60 grains.
Water	2 fluid ounces.
Ammonia, till the solution is blue.	
Potassium sulphide	120 grains.
Ammonia	3 fluid drachms.
Water	$1\frac{1}{4}$ fluid ounces.

This solution gave precisely the same results as with potassium sulphide and water, so that the other constituents appear to be useless. The reaction on copper is instantaneous, but brass is simply tarnished.

§ 112. The following solutions containing a mercury

salt are said to yield good results, but the author could only obtain indifferent colours and cannot recommend the method :—

Mercury chloride	150 grains.
Ammonium nitrate . . .	150 ,,
Water	3½ fluid ounces.

Ammonia, till the precipitate formed redissolves.

After pickling the work in the above solution, the operator is then advised to immerse it in a solution of ammonium sulphide or potassium sulphide.

The mercury solution behaves like a quicking solution as used by electroplaters. Both copper and brass are instantly coated with mercury when immersed in it.

A brass tray first coated with mercury in this way and then immersed in the sulphide solution was darkened upon its surface, but on scratch-brushing the mercury was partly exposed.

A coppered tray blackened instantly on immersion in the sulphide bath, but became nearly white on scratch-brushing. The black surface may be preserved by omitting the scratch-brushing and simply drying on a hot plate. The black colour on the copper is doubtless due to a deposit of copper sulphide, and possibly a little mercury sulphide, for if the black colour was due to mercury sulphide only, one would expect the mercury-coated brass to blacken as readily as the mercury-coated copper, but this is not the case. Better results can be obtained upon copper by omitting the mercury solution and using the sulphide bath only. The effect of these solutions upon brass is of no practical utility.

Another solution containing a mercury salt consists of—

Mercury sulphide	50 grains.
Potassium ,, ...	50 ,,
Sodium hydrate (20 per cent solution)	1 fluid ounce.
Water	3 fluid ounces.

The following results were obtained :—

(*a*) Brass tray . . .	dark brown and patchy.
(*b*) Coppered tray . .	gray-black.
(*c*) ,, ,, . . .	quite black.

The colour on (*a*) was only obtained with considerable difficulty, and a second attempt to produce an identical result failed completely. From this it may be inferred that brass can only be coloured in this solution when it is freshly prepared and nearly concentrated. The colour even then is very poor, and practically worthless.

A copper tray blackens immediately after immersion, and then presents a fine velvet-black surface which is easily rubbed off, leaving a gray-black appearance. The jet-black colour can be preserved by rinsing the article in alcohol, igniting the latter, and coating the article with zapon lacquer.

In this case results equally as good can be obtained by omitting the mercury sulphide and sodium hydrate, and using only the potassium sulphide and water. It is probable that mercury sulphide has very little influence in the production of the black colour, and that the effect is almost entirely due to the potassium sulphide acting on the copper and producing the black copper sulphide, as before described.

§ 113. The following solution is recommended for producing a steel-blue colour on copper :—

Potassium sulphide	20 grains.
Sodium chloride	20 ,,
Water	1 pint.

A copper ash-tray received a colour which was not a steel-blue but rather a gray-black. This solution behaves much the same as potassium sulphide alone without the sodium chloride.

§ 114. Böttger states that a solution of potassium sulphantimoniate imparts a beautiful and durable coating to copper. He was occupied for some time experimenting, so as to produce a coating of sulphide on the surface of copper vases and similar articles in order to give them a pleasing appearance, and enable them to resist the action of the atmosphere. Such a coating we have already seen can be obtained by means of potassium or ammonium sulphide. The present solution is said to impart a brilliant grayish-blue colour, of a shade intermediate between the gray of platinum and the gray of steel.

The difficulty is to protect the metal completely from all superficial oxidation on immersing it in a nearly boiling solution of the sulphantimoniate. If several articles are suspended at the same time they must not touch each other, or the sides of the containing vessel. When the articles have assumed the proper tone, which takes some time, they are well swilled with water and dried with a linen cloth.

In case the operator has no potassium sulphantimoniate at hand, which decomposes somewhat readily, the following mode of preparing a similar solution is recommended, and is both simple and economical. Mix together 4 parts by weight of dry sodium sulphate, 3 parts of finely powdered antimony sulphide, and 1 part of

powdered charcoal, introduce the mixture into a crucible which has been previously made red-hot, cover with a lid, and when all action has ceased pour out the mass. Place in a vessel with sufficient water, add $\frac{1}{2}$ part of flowers of sulphur, boil for some time and filter off the insoluble residue. The clear liquid, when further diluted with water, is ready for use.

A solution for testing this substance as a bronzing agent was made by dissolving 25 grains of potassium sulphide in 3 fluid ounces of water, and saturating the hot solution with freshly precipitated antimony sulphide. The following results were obtained :—

(*a*) Brass tray	rich shellac-brown.
(*b*) ,, ...	,, ,, but paler.
(*c*) Coppered tray . . .	dark blue-black.
(*d*) ,, . . .	steely-brown.

The solution acted on brass very slowly; (*a*) was produced in about fifteen to twenty minutes, (*b*) occupied at least half an hour and was not so good as (*a*). The result in the second case may be due to the solution having altered in the interval. Both were scratch-brushed at intervals and re-immersed in the solution. The tray (*b*) was not bronzed until after (*d*) was finished.

The reaction of this solution on copper is almost instantaneous. The metal assumes various shades from nut-brown to blue-black, according to the thickness of the deposited film. If the copper is immersed too long or the solution used too hot, the coating is not adhesive. The coloured film produced by this solution is probably a mixture of copper sulphide and metallic antimony. This mixture is useful in giving dark tints to copper differing

slightly from those obtained by the agency of potassium or ammonium sulphide alone, in that the reddish-black tone obtained in their solutions gives place to a grayer-black in the sulphantimoniate solution.

§ 115. A dark colour on copper may be obtained by immersion, or by painting the following liquid on the articles :—

Arsenic oxide	120 grains.
Hydrochloric acid	½ fluid ounce.
Sulphuric acid	60 ,, grains.
Water	3 ,, ounces.

The solution works quickly both on copper and brass, but does not produce a pure black on either ; the deposit of arsenic has a dark gray colour, which becomes lighter on scratch-brushing. If copper is dipped momentarily into the solution it receives a very thin transparent film of arsenic, which on scratch-brushing presents a pinkish-gray colour, as on (*b*). The following results were obtained :—

(*a*) Brass ash-tray . . .	deposit of arsenic.
(*b*) Coppered ash-tray . . .	film of arsenic.
(*c*) ,, ,, . . .	deposit of arsenic.

§ 116. The following solution is recommended for obtaining a deep black colour on copper and its alloys :—

Copper nitrate	100 parts.
Water	100 ,,

The above salt is dissolved in the water and the article, if large, is painted with it, if small, the article may be immersed in the solution. It is then heated over a clear coal fire and lightly rubbed. The article is next placed

in or painted with a solution of the following composition :—

Potassium sulphide	10 parts.
Water	100 ,,
Hydrochloric acid	5 ,,

We have obtained more uniform results by using a solution about three times more dilute than the above, viz. :—

Copper nitrate	100 parts.
Water	300 ,,

Small work can be much more conveniently treated by immersion in the solution, and after draining off or shaking off the excess of the solution to heat the work on a hot plate until the copper salt is decomposed into the black copper oxide. It would be difficult to heat large articles upon a hot plate, but a closed muffle furnace should give better results than an open coal fire. In any case the heating process should not be continued longer than is necessary to produce the change mentioned above.

A good black can be produced upon brass in this way without the aid of the potassium sulphide solution, which imparts a bluish tint to the copper oxide. The black coloration does not appear to adhere so firmly to copper as it does to brass, and, considering this circumstance, it is probable that the subsequent immersion of blackened copper work into the potassium sulphide is an advantage.

§ 117. A great variety of shades of brown may be produced on copper by a barium sulphide solution, beginning with a tone only a little darker than copper itself and

passing through crimson to light brown, and then through a succession of darker shades until a very dark brown, nearly black, is reached.

It appears difficult to obtain the crimson colour uniformly distributed over the surface of the work, so that this method cannot be recommended for that colour. The brown colours, however, are very rich in tone, and very easily produced in almost any required shade, and their distribution is practically uniform. The bronzed surface will also stand a severe scratch-brushing, and is, in fact, improved by that process, but rendered a little lighter in tone. It is well, therefore, to produce a colour in the solution a little darker than that required upon the finished work.

The effect produced upon work having relief parts can be heightened by rubbing those parts, after bronzing, with a wet cork which has been dipped in silver sand, so as to expose the underlying metal, in which condition the work may be finished. If it is preferred, after treating the metal in the manner just described, it may be immersed momentarily in the bronzing solution until the exposed copper takes a different shade of colour to that upon the general surface of the work, when the whole may be scratch-brushed and finished.

If the solution is strong—say 100 grains of barium sulphide to 1 pint of water—and hot, a black colour is imparted to copper immediately after immersion, but if the solution is used cold, this result is only achieved after some time. A dilute solution, containing say 25 grains of the sulphide to 1 pint of water, can be more easily controlled, and the process arrested at any required stage of coloration.

PRODUCTION OF A GREEN BRONZE ON COPPER AND BRASS

§ 118. Reference has already been made at some length to the formation of a green patina on copper and its alloys by the slow and continuous action of air and moisture, extending over lengthened periods of time. It is not surprising then that attempts should be made to imitate the effects of nature by artificial means and to impart to copper and copper alloys similar beautiful effects.

This may be brought about in a variety of ways, with the formation of the so-called antique patina, varying in tone from dark brownish-black to dark greenish-black, also from yellowish-green to bluish-green; and these different shades being capable of production in different parts of the same article, a great variety of shades may be generated. Thus a dark greenish-black may be formed on the groundwork, with a bluish or yellowish-green on the parts which are in high relief.

The bluish-green patina is formed by the action of basic copper carbonate, and the yellowish-green by the action of basic copper chloride, so that if one wishes to imitate the natural colouring use must be made of reagents containing similar ingredients. The action may be re-

ferred to the influence of carbonic acid and chlorine respectively upon copper oxide. The slower the action the more beautiful and lasting will be the effects, so that a very dilute solution of a copper salt, or a very dilute or weak acid, acting for a considerable period of time on copper or a copper alloy, will give better results as a rule than a more rapid action by means of a stronger solution.

If a weak solution is painted on to the metal by means of a brush or dabbed on the surface by means of a cloth or sponge a slight stain is imparted which facilitates the subsequent colouring. A judicious and thorough scratch-brushing will then be a great advantage to secure that uniformity of surface, without which the final effect will be considerably marred.

The solution must not be too cold or the liquid will not be uniformly distributed, thus causing an uneven and patchy appearance; nor must it be too hot or it will dry up too quickly and simply leave a loose deposit which will readily peel off, in consequence of the surface of the metal not being sufficiently corroded by the acid liquid, as is the case when the action is more prolonged. A suitable temperature is about 20° C. both for the article to be bronzed and the solution which is to be applied to it.

It is an advantage in many cases to impart to copper articles a dark tone at first by means of a sulphur compound, such as ammonium or potassium sulphide solution, which should be very dilute so as to yield only a very thin coating, for if the sulphide deposit is too thick the metal will not take the desired green patina. It is desirable in some cases to produce different shades of colour in different parts of the same article—for example, to have a dark groundwork and green on the relief parts, when

the advantage of the primary sulphide deposit will be apparent.

Instead of using saline solutions to produce the antique green rapidly, the colour may be obtained by submitting the articles to the same chemical conditions and influences as those developed upon them by air and moisture during a long period of time. The green patina consists, as already stated, of a hydrated copper carbonate similar to the natural minerals malachite and azurite, and it is probable that they are formed in the same manner. The surface of the metal is first oxidised by the agency of air and water, and the oxide thus formed slowly combines with carbonic acid, forming copper carbonate mixed with copper hydrate.

§ 119. Elsner imitates this natural method by introducing carbonic acid gas through an aperture into an earthen vessel, in the bottom of which has previously been placed a solution of common salt. Then the perfectly cleaned article is first plunged into a mixture of equal parts of vinegar and water, and when every portion has been perfectly moistened, it is suspended in the vessel which is filled with the moist carbonic acid. The mouth of the vessel is then tightly closed and the aperture which conveyed the carbonic acid plugged up. The article is suspended by means of a copper wire.

The whole apparatus is allowed to stand for several weeks, when the object is found to be coated with a bluish-green patina in the deep parts, and has all the appearance of a body which has been exposed for many years to atmospheric influences. This patina afterwards perfectly resists the action of the air without showing any signs of change. The longer the process is allowed to

continue the more beautiful is the patina, and the more it resembles the natural product. It is necessary to avoid the employment of too strong a solution of vinegar, for, although the stronger the vinegar the more rapid the oxidation, yet the more easily will it be dissolved afterwards by atmospheric moisture.

If the carbonic acid which is employed contains a very small proportion of sulphuretted hydrogen (which may be generated simultaneously with the carbonic acid by adding a small quantity of iron sulphide to the calcium carbonate used to generate the carbonic acid) then the surface of the article quickly assumes a particular brown colour, and very soon afterwards the green patina begins to form. The advantage of this primary brown coating has been previously referred to.

A quicker method than the above is to put the article in a box, and on one side of it to place a vessel containing water to produce moist air, and on the other a vessel containing dilute hydrochloric acid, into which, from time to time, bits of marble or chalk are dropped to generate carbonic acid. An antique patina is produced more readily on copper containing tin or zinc alloyed with it than on pure copper. Copper containing much arsenic, which has been bronzed green, will in time turn black, and this is even the case with copper alloys containing much arsensic, therefore it is advisable to use as pure metals as possible.

§ 120. Articles of bronze which are exposed to the atmosphere of a large town soon become discoloured by the various gases generated by the manufactories and by the products of decomposition which pass into the air from the combustion of gas and coal. This imparts to them a dirty black appearance instead of an artistic bronze

colour. The Society for the Encouragement of Arts, Berlin, in 1864 made an investigation into this subject and performed a number of comparative experiments with a view of finding a remedy.

"They first sought to settle the question as to whether a certain definite composition of the alloy favoured the formation of a beautiful patina. For this purpose they placed in different localities some bronze works, remarkable for a beautiful patina on the surface, the metal of which had been previously analysed. The analyses proved that the bronzes had a widely different composition. The proportion of copper varied from 94 to 77 per cent; that of tin from 1 to 9 per cent. In others the tin did not exceed 4 per cent; while in some cases the amount of tin was not more than ·8 per cent, while it contained up to 19 per cent of zinc. Other metals present were considered as accidental impurities, such as lead, iron, and nickel.

"With all this variety in composition each of the bronzes nevertheless had received a very beautiful green patina. It was thought possible that the composition would exercise an influence on the duration of the time which the bronzes, all other circumstances being equal, would require to become coated with the patina; but the experiments did not leave any doubt on the mind that the patina was formed on alloys of the most varied composition.

"In order to discover what other influences might determine the formation of the patina, they placed a number of bronze busts in a part of Berlin where many particularly objectionable exhalations were sent into the atmosphere, and where different statues exist in the neigh-

bourhood without any trace of a green patina, but were covered with the dirty black coating before referred to.

"Observing upon several monuments, in the parts most accessible to the public, and which are liable to be frequently touched by the hands, that there was not only a green patina, but a special patina of the most valuable properties, while the other parts were black and non-uniform. The commission charged with these researches conjectured that it was presumable that the greasy matter of the hands played an important role in the formation of the green patina. In consequence of this, one of the exposed busts was syringed with water each day, except when it rained, so as to keep it quite clean. Besides this, it was treated with bone oil, once a month, by means of a paint-brush, and then rubbed with a linen cloth. A second bust was equally well cleaned every day, but without any periodical oiling. A third bust was also washed in the same way, but treated with oil only twice a year. A fourth bust, for the sake of comparison, was exposed but neither washed nor submitted to any treatment. The result of these trials was to prove in the most unequivocal manner that the conjecture as to the effect of grease was correct.

"The bust which had been oiled once a month assumed a dark green patina, which was declared by connoisseurs to be very beautiful. That which had been oiled twice a year had a less beautiful appearance. That which had been simply washed with water presented none of the beautiful features acquired by the formation of the patina. Lastly, that which was left untouched had a dull appearance, and was of a dark colour.

"We may consider it as certain that a bronze article

which is exposed to the air, and which has been cleaned once a month, and afterwards rubbed with oil, will become coated with a beautiful patina.

"With regard to this periodical rubbing with oil, it would manifestly be unadvisable to treat large monuments too often, and it was for this reason that the experiments to determine the effect of treatment twice a year were performed. The Berlin Commission also tested two new bronzes which had received a patina by artificial means with the use of certain chemical reagents, in order to assure themselves how these would comport themselves by analagous treatment.

"The manner in which the oil acts in inducing the formation of the patina is difficult to determine. The experiments, however, have demonstrated that it is necessary to avoid excess of oil, and that it should be rubbed off as far as convenient. If the oil is in excess, it attracts dust, and the bronze takes a poor appearance. It cannot be supposed that the minute quantity of oil that remains forms a chemical combination with the layer of oxide of the bronze, since bone oil was shown by the experiments to be as advantageous as olive oil. It is probable that the minute layer of oil has no other effect than that of preventing the deposition and adherence of moisture, which so easily fixes the dust, absorbs gases and vapours, and in which vegetation is so frequently developed. In every case in these experiments, whatever the mode of action, it was abundantly proved that greasy matter contributed to the formation of the patina.

"It is possible that this gradual formation of a patina may be useful for other work under different circumstances. We have observed that on bronzes covered with a beautiful

patina, in the points where water has run over them, a pale, chalky dulness, which with time increases in thickness. A convenient treatment with oil would probably prevent the formation of this layer, but it can only be decided by prolonged experiments.

"This method of the employment of oil for preserving and beautifying bronze work leads one to hope in the future the public monuments in large towns will be clothed with a brilliant patina. This patina, in the localities where coal is exclusively used as the combustible, will not be a bright green, it will appear deep coloured, perhaps even blackish, but it will possess all the other choice properties in the patina, and in particular the brilliant property of reflection from the surface."

DIFFERENT METHODS OF PRODUCING AN ANTIQUE PATINA

§ 121. For the production of a yellowish-green bronze the following solution may be employed :—

Vinegar	1 quart.
Ammonium chloride	250 grains.
Common salt	250 ,,
Liquid ammonia	½ ounce.

The two salts are first dissolved in the vinegar and the ammonia added to the solution, when it is ready for use. Small articles may be immersed in the solution, then removed, and when one part begins to dry, a paint-brush drawn over it so as to keep all parts uniform. The operation is then conducted as described for large work. Large articles, which cannot be dipped in the solution, are coated with the bronzing liquid by means of a paint-brush. The

surface of the article must be entirely covered as uniformly and as rapidly as possible, taking care to keep every part moist. In a few seconds the solution begins to colour the body with a green stain, the copper changing in tint, and a greenish froth begins to form. The workman must now, without dipping his brush again in the solution, proceed to spread the colour all over, carefully following the contour of the ornamental parts.

When the copper has taken a convenient tint, and the liquid begins to dry and to thicken, the wet parts should be dried with another brush having long bristles or hairs, and when this is too wet to use, another, and so on till the whole is dry. The article is then allowed to rest in a warm place till the next day, when a second coating is given in the same manner as the first. The colour now assumes a deeper tone, and it may be necessary to repeat the operation several times to get a desired shade. After allowing the article to remain twenty-four hours after imparting the last coat, it is finished by well brushing with a soft brush which has been rubbed on a cake of white wax. It is always advisable to leave each coating for an interval of twenty-four hours to act on the metal, but some operators only allow an interval of six hours.

It sometimes happens that the base or other parts of an object are of brass, while the other parts are made of copper; in such a case the brass parts take a paler tint than the copper. The tints may be equalised by means of a little plumbago which is rubbed on the pale parts by means of a soft short bristled brush. If it is desirable in any case to quicken the process, the amount of ammonium chloride and common salt may be doubled for the same quantity of liquid in giving the second coat.

§ 122. The following solution may be employed for producing a yellowish-green patina :—

Ammonium chloride	155 grains.
Copper acetate	78 ,,
Water	16 ounces.

To test this solution the liquid was painted on the work, and was found to yield better results than by immersion. The same precautions were taken as those described in the previous paragraph, allowing an interval of twenty-four hours between each application. The following are the results:—

(*a*) Cast copper . .	light brown on the high parts and bluish-green on ground.
(*b*) Cast brass . .	drab colour on prominent parts and bluish-green on ground.
(*c*) Stamped brass . .	very patchy, bluish-green only in parts where liquid was thick.
(*d*) ,, coppered	light brown colour in some parts and bluish-green patches in others.

Three separate coats were given to each and the colour became darker and denser after the third coat. Cast work appears much better adapted for this bronze than stamped work. The colour, after the first two coats, appeared a yellowish-green, but after the third application it became much darker in tone and decidedly bluish-green.

§ 123. A solution of a complicated nature is given by Buchner as a suitable medium for producing a green patina. The liquid is recommended to be applied by means of a brush or a sponge, allowing to dry, and repeating until the desired colour is reached. It is said to be best to put the painted articles into a closed chamber to dry. In the same chamber is placed a vessel containing

dilute hydrochloric acid and vinegar and some pieces of marble. By the reaction of these substances on each other carbonic acid is generated, which favours the formation of the antique patina. Should the patina become too blue then the article is to be painted with a solution of 120 parts of ammonium carbonate and 40 parts of ammonium chloride dissolved in 1000 parts of water. The bronzing solution recommended is—

Ammonium chloride . . .	78 grains.
Cream of tartar	78 ,,
Copper nitrate	720 ,,
Hydrochloric acid	6 drachms.
Water	16 fluid ounces.

The above solution was tested by the author in the same way as in his preceding experiments without obtaining any useful effects.

(*a*) Cast copper . . .	dirty brown colour, with one or two small patches of green after third painting.
(*b*) Cast brass . . .	dark drab colour, with faint green shade after third painting.
(*c*) Brass ash-tray . . .	dark patchy drab colour, with faint green shade after third painting.
(*d*) Coppered ash-tray . .	terra-cotta patchy colour but no green patina after third painting.

From these experiments it may be concluded the solution is useless by itself for producing a green colour on copper and brass.

§ 124. The following solution yields fairly good results both on copper and brass :—

Ammonium carbonate . . .	155 grains.
Oxalic acid	78 ,,
Vinegar	16 fluid ounces.
(*a*) Cast copper . . .	yellowish-green on groundwork and crevices of the design, the other parts were a dark drab, with pale film of yellowish-green after the third coat.
(*b*) Cast brass	same as on cast copper.
(*c*) Stamped brass . . .	,, ,,
(*d*) ,, coppered .	,, ,,

§ 125. The solution referred to in this paragraph yields a pale green patina on brass and copper much more uniformly distributed over the surface of the metals than that produced on the same metals by the solution described in the former paragraph.

Ammonium chloride . . .	124 grains.
Common salt	124 ,,
Ammonia	4½ drachms.
Water	16 fluid ounces.

The patina on the cast brass and cast copper was about the same, so that these metals seem to be equally adapted to receive a light green patina by this solution. A brass ash-tray was well covered, but a coppered ash-tray had a reddish-brown colour on the raised parts. In each case the deep parts had received a denser deposit. Three coats were given to each article.

§ 126. A very dark bluish-green patina can be obtained by using a solution of

Ammonium carbonate . . .	1163 grains.
Sodium chloride	380 ,,
Copper acetate	460 ,,
Cream of tartar	380 ,,
Water	16 fluid ounces.

(*a*) Cast copper . . .	bluish-green.	
(*b*) ,, brass . . .	,,	but paler.
(*c*) Stamped brass . . .	,,	,, and patchy.
(*d*) ,, ,, coppered .	,,	,, ,,

The groundwork of (*a*) was a very dark bluish-green after the third application of the solution and drying. The raised parts were brown, with only a shade of green. (*b*) was similar to (*a*) with regard to distribution, but the blue of the deep parts was of a lighter shade; (*d*) was bluish-green on the groundwork and intricacies, and reddish-brown on the prominent parts.

§ 127. An excellent yellowish-green patina may be obtained by using the following solution, as shown by the experiments below :—

Ammonium chloride . . .	124 grains.
Potassium oxalate . . .	31 ,,
Water	16 fluid ounces.

(*a*) Cast copper	yellowish-green.
(*b*) ,, brass	,,
(*c*) Brass ash-tray	,,
(*d*) Coppered ash-tray . . .	,,

(*a*) was coated a light yellowish-green all over, but denser in the deep parts; (*b*) was very good on the groundwork, but not so good as (*a*) on the raised parts; (*c*) was yellowish-green on the groundwork, and a brownish-drab on the prominent parts; (*d*) was yellowish-green on the groundwork and reddish-brown on the raised parts. This article was somewhat patchy, the others, especially the cast copper, fairly uniform.

§ 128. The following solution yields results of a uniform character, after two or three applications with subsequent drying :—

Ammonium carbonate . . .	900 grains.
,, chloride . . .	300 ,,
Water	16 ounces.

The solution was painted on the work as in the previous cases, and it was then allowed to remain twenty-four hours before the second application, and the same time between the second and third. The following results were obtained :—

(*a*) Cast copper .	bluish-green patina on groundwork.	
(*b*) ,, brass . .	,,	,,
(*c*) Stamped brass tray	,,	,,
(*d*) Coppered tray .	,,	,,

(*a*) was yellowish-green after the second coating, but became bluish-green after the third application. The green of the groundwork was fairly uniform, but the more prominent parts were brown with a greenish tint. (*b*) was scarcely affected by the first coating of the solution, after the second it turned yellowish-green, and after the third a bluish-green colour appeared on the groundwork, but of a lighter shade and less dense than that on the cast copper ; (*c*) acted throughout much the same as (*b*) ; (*d*) was yellowish-green after the second coating, but assumed a bluish-green in the deeper parts, with brown on the raised parts, after the third application of the solution and drying.

§ 129. The following mixture is equally good with the last, and acts much in the same way, producing a bluish-green patina after three applications of the solution and subsequent drying :—

Ammonium chloride . . .	770 grains.
Alum	370 ,,
Arsenious oxide	160 ,,
Vinegar	16 fluid ounces.

The method of conducting the experiments was the same as in the previous ones—

(*a*)	Cast copper . . .	bluish-green and uniform.
(*b*)	,, brass . . .	,, ,,
(*c*)	Stamped brass . .	,, but patchy.
(*d*)	,, coppered .	,, ,,

This solution is reliable and produced excellent results on cast work, but is not so good for stamped work.

§ 130. A good solution for yielding a yellowish-green patina on cast copper and cast brass work is composed of

Copper nitrate . . .	1500 grains.
Sodium chloride . . .	1500 ,,
Water	16 fluid ounces.

The conditions of its application to the work and the subsequent treatment are the same as before described. The following results were obtained :—

(*a*)	Cast copper . . .	yellowish-green.
(*b*)	,, brass . . .	,,
(*c*)	Stamped brass . .	,, but patchy.
(*d*)	,, coppered .	light brown, with green patches.

(*a*) was green on the groundwork and brown on the prominences; (*b*) was green on the groundwork and brownish-drab on the upper portions; (*c*) was drab in places, the other parts were green; (*d*) was green and reddish-brown in different parts. The bottle containing the liquid should be well shook up before applying the liquid to the work.

§ 131. Buchner recommends the following solutions for producing a patina on electro-deposited copper :—

I. A 20 per cent copper nitrate solution.
II. A solution of ammonium sulphide.

III. A 20 per cent solution of calcium chloride.
IV. Bromine water (30 parts bromine in 970 parts water).

A. He mixes equal volumes of I., III., and IV. to form a suitable solution for bronzing, especially for electro-deposited copper, which takes different shades according to the treatment. He then dips a perfectly cleaned figure in this solution for one or two minutes, removes, and allows the liquid to dry on the work without swilling, which gives it a pale bronze tone which in the light is first greenish, then a yellow bronze tone. After allowing to dry it is again immersed in the solution, and after the second drying it assumes a beautiful green patina of a dead lustre, which may be made more beautiful by brushing with a waxed brush.

If, after one or two minutes' immersion, the article is swilled with water and dried by rubbing between sawdust, it has a browner tone, which somewhat darkens on exposure to light, becoming at first greenish, then brownish-black.

B. The tone may be modified by using a mixture consisting of two volumes of the solution No. I., one volume of the solution No. IV., and one volume of the solution No. III. The greater the proportion of the copper solution the darker will be the tone. The more bromine and calcium chloride is used the lighter will be the tone produced. The coloration depends upon the production of cuprous oxide in its different modifications, from yellow to dark brown, along with some cuprous bromide and cuprous chloride, which undergo darkening by the action of light.

If the article which has been coated according to either of the directions given in A or B is, after drying, placed

in an atmosphere of sulphuretted hydrogen gas, or in the vapour of ammonium sulphide, taking care not to have too saturated an atmosphere, then only the outer surface-film will be changed into copper sulphide, which will be a grayish-black. If now the article is immersed in a solution consisting of two parts of No. I., two parts of No. IV., and one part of No. III., taken out and allowed to dry at the ordinary temperature, it will receive a beautiful greenish-black groundwork like antique bronze, with a copious patina in the recesses in the lapse of half an hour. The coloration is so firm that the article may be brushed with a waxed brush.

It is necessary for success that the preliminary coating of sulphide should not be too thick. It should be pale brown to grayish-brown. If it is a dark colour, almost black, the coating will probably be too thick to take any green patina at all. Buchner states, with respect to the foregoing method, that a more beautiful effect, in so short a time, cannot be obtained by any other method so far as he himself knows.

§ 132. The following solution is said to yield a good yellowish-green patina on copper and brass. The appended results were obtained after three applications, with an interval of twenty-four hours between for drying :—

Copper nitrate	1000 grains.
Zinc chloride	1000 ,,
Water	12 fluid ounces.

The above liquid was painted on to the work with a brush, allowed to remain some time to act on the metal, but not sufficiently long to allow any part to dry. It was then wiped off with a brush, so as to leave a thin but uni-

form film of solution, and allowed to stand for a day. The operation was then repeated.

(*a*) Cast copper-plate . . .	very pale greenish tinge.
(*b*) Cast brass-plate . . .	,, ,,
(*c*) Brass stamped tray . . .	just stained.
(*d*) Coppered stamped tray . .	terra-cotta colour.

The plate (*b*) was only very slightly tinted green after three applications. Neither (*a*) nor (*b*) was of any practical value, and the method could only be employed when a considerable number of repetitions is admissible. For stamped work it appears quite unsuitable.

§ 133. The following solution has been strongly recommended for producing a good yellowish-green antique bronze on copper, but the author could not get any satisfactory results, as in the case of other solutions in which a mercury salt is a constituent. The quantities employed were—

Copper nitrate	150 grains.
Zinc sulphate	200 ,,
Mercury chloride	200 ,,
Water	16 fluid ounces.
(*a*) Cast copper . .	exceedingly thin and pale green film.
(*b*) Cast brass . .	practically unaltered.
(*c*) Brass stamped tray	coated with mercury.
(*d*) Coppered ,, .	similar to the cast copper.

The experiments were not continued after the third repetition.

§ 134. A very good antique green was obtained by the following mixture :—

Copper carbonate	3 ounces.
Ammonium chloride	1 ounce.
Common salt	1 ,,

Cream of tartar	1 ounce.
Copper acetate	1 ,,
Vinegar	8 fluid ounces.

The above is from an old French recipe, and although the result is very good there are unnecessary constituents, as the same effects may be produced by a much simpler mixture. The proper quantity of copper sulphate was dissolved in water, and sufficient sodium carbonate was added to precipitate the copper as carbonate. The whole was allowed to stand until the precipitate settled down, when it was filtered off, washed, the vinegar added, and the other substances mixed with it. A portion of the mixture was then applied to the articles with a brush as usual, and then allowed to rest for twenty-four hours, when the operation was repeated, and so on a third time.

(*a*) Cast copper	bluish-green.
(*b*) ,, brass	,,
(*c*) Stamped brass	,,
(*d*) ,, ,, coppered . . .	,,

The results were good in each case. After the first application there was no apparent change except a tarnishing of the metal; after the second application there was a pale yellowish-green film; and after the third a good bluish-green patina on the surface. The stamped trays, (*a*) and (*b*), were first tarnished by immersion in a solution of potassium sulphide, and then the first coating of the present solution was given, but no advantage appeared to be gained by this preliminary treatment.

When the right degree of green has been obtained, the article may be finished by rubbing the surface lightly with a cloth which has been moistened with olive oil,

when the green colour becomes more transparent in the rubbed parts.

§ 135. According to Kayser, a greenish-brown colour on copper may be obtained by first staining the surface of the article with a solution of potassium sulphide, which, after drying, is moistened with a solution of ammonium chloride, vinegar, and ammonia. The following proportions were tried :—

Ammonium chloride . .	80 grains.
Ammonia	3 drachms.
Vinegar	to neutralise the ammonia.
Water	16 ounces.
(*a*) Cast copper	very pale bluish-green.
(*b*) Cast brass	,, ,,
(*c*) Stamped brass . . .	,, ,,
(*d*) ,, coppered .	simply a reddish-brown.

A considerable number of repetitions would be required to get any useful effect. The process was repeated three times in the above experiments.

§ 136. The following solution is due to G. Buchner, and yields very good results, even after the first treatment. The following proportions were used by the author :—

Copper nitrate	48 grains.
Ammonium chloride . . .	48 ,,
Calcium chloride	48 ,,
Water	3 fluid ounces.
(*a*) Cast copper	yellowish-green.
(*b*) ,, brass	,,
(*c*) Stamped brass	,,
(*d*) ,, copper	,,

All the above assumed the green patina on drying after the first coating. The colour was uniform all over, and

appeared as good after the first as after the third application.

§ 137. The use of bromine water added to a copper solution has been recommended for imparting an antique patina, but the author could obtain nothing more than a stain on brass and copper by either of the two following solutions :—

1	Copper nitrate	96 grains.
	Calcium chloride	96 ,,
	Water	2 ounces.
	Bromine water	1 fluid ounce.
2	Copper nitrate	96 grains.
	Calcium chloride	48 ,,
	Water	1½ fluid ounces.
	Bromine water	½ fluid ounce.

It may be stated as a general rule that in all the foregoing cases where copper nitrate is recommended as a constituent of a bronzing solution, the blue deposit which forms at the bottom of vessels, containing old aquafortis or pickle, which has been used for dipping brass or copper goods, may be employed, and as in many cases this deposit is thrown away, it is of course a great saving to employ it instead of new copper nitrate.

BRONZING OF COPPER ALLOYS

BRASS [1]

§ 138. By this term is meant all alloys of which copper and zinc are the essential and chief constituents, but more generally the name is confined to those alloys which have a decidedly yellow colour. Different qualities of brass are known in commerce by a variety of names which have given rise to great confusion as to their particular meaning, seeing that brass sold under the same fanciful names has a wide difference in properties and composition, while, on the other hand, many different names are given to the same alloy in different localities. Dr. Percy mentions "that the terms *tombac*, *prince's metal*, *similor*, and *Mannheim gold* are all represented to contain 85 per cent copper and 15 per cent zinc." The alloys termed *oreide* vary from 90 per cent copper and 10 per cent zinc to 80 per cent copper and 20 per cent zinc. The term "tombac" is made to answer for alloys containing from 99 to 70 per cent of copper and 1 to 30 per cent zinc.

Commercial brass never consists entirely of copper and zinc, since whatever impurities exist in the separate metals will also be found in the alloy, the most common of these

[1] See author's work on *Mixed Metals*, p. 80, Macmillan and Co

being lead, iron, arsenic, and tin. It often happens that some of these are purposely added to produce a certain effect, as lead, for example, in cast brass. The colour of brass shows great variations, according to the proportions of the constituents, ranging from the red of copper at one end to the bluish-white of zinc at the other, but the change from red to white is by no means uniform.

Thus, alloys containing 94 to 99 per cent of copper are red, with only a faint yellow tint; with 87 to 93 per cent of copper the colour is reddish-yellow; from 79 to 86 per cent of copper a yellowish-red tint prevails; below this, down to 74 per cent of copper, the alloys are yellow; with a content of 67 per cent of copper a reddish-yellow tint is obtained; with 60 to 66 per cent of copper the colour is a full yellow; with 59 per cent of copper a reddish colour is obtained; with 52 per cent of copper the colour is nearly golden-yellow; with a less amount of copper than the above the colour of the zinc begins to overpower the red colour of the copper, the alloys becoming more lead-like in appearance as the proportion of zinc increases.

For rolling into sheets it is essential that the alloying metals should be practically pure, and that the alloy should consist only of copper and zinc. One of the most injurious substances to brass is antimony, which is occasionally found in common copper. Lead, arsenic, tin, and iron are occasionally present in very small quantities. The composition of sheet and stamped brass varies from 92 to 65 of copper to 8 to 35 of zinc.

The composition of cast brass varies considerably, and depends to a large extent on the uses to which the cast articles are to be put, as also with the particular shade of

colour it is desired to obtain. Thus the various alloys for jewellery having a reddish-yellow colour are composed of 82 to 90 per cent copper and 18 to 10 per cent zinc; while those with a full yellow colour contain 60 to 70 per cent of copper and 40 to 30 per cent of zinc. Lead from 1 to 2 per cent is a usual constituent of cast brass, while iron and sometimes tin are present as impurities. Very common cast brass made from old materials, such as scrap and brass dust, often contains a variety of ingredients besides copper and zinc. The composition of some French fine brass castings is given below—

	I.	II.	III.	IV.
Copper . .	63·7	64·45	70·90	72·43
Zinc . . .	33·5	32·44	24·05	22·75
Lead . . .	2·5	·25	2·00	1·87
Tin . . .	·3	2·86	3·05	2·95

From the foregoing description of the nature of brass, which may vary so widely in the amount and nature of the constituents, it will be easily understood that these different alloys will not behave the same in the colouring bath, and that the various shades of colour may differ according to the composition of the alloys.

Zinc alone is only capable of assuming a very limited number of shades of colour, and these are generally gray or black, while copper, on the other hand, is competent to take on an almost infinite variety of tints from pale yellow to jet-black. It by no means follows that because a certain solution colours copper it will also colour brass, as the zinc may so modify the properties of the copper as to prevent any notable change taking place. In some cases

brass articles will assume a beautiful colour in a given solution which is quite neutral to copper. This may be due to the galvanic action set up between the copper and zinc producing greater chemical activity than when the electrical agency is absent.

It is stated by Buchner that, with respect to the action of copper-zinc alloys, when the proportion of zinc does not exceed 50 per cent the colouring action of the copper predominates, and that copper salts are only precipitated with difficulty in an acid solution, while alloys with over 50 per cent of zinc partake more of the character of zinc, and that copper salts are easily precipitated in an acid solution.

The colouring effect on a sample of brass may be modified by the preliminary cleaning treatment it has undergone. The acid or alkaline liquids acting unequally on the components of the alloy will produce a surface of a different composition to that of the bulk of the metal, so that two samples of the same alloy will often exhibit different shades of colour. I have often observed this effect with specimens which have been bronzed several times and have had the coloured film dissolved off so as to try the effect of a different solution on the same metal.

If brass is placed in a solution of ammonia it becomes paler in colour after a time by the dissolving of the copper, but if a sample of the same alloy is treated with hydrochloric acid the zinc is largely dissolved, leaving the alloy richer in copper. Such specimens when subsequently immersed in certain bronzing solutions will exhibit different shades of colour.

§ 139. Brass articles may be made to receive all the colours which can be produced on copper by first coating

them with a layer of copper by electro-deposition; or by wrapping them round with iron wire and placing them in a very dilute solution of sulphate or nitrate of copper; or by immersing them in a solution of copper chloride, and heating them to a temperature of about 150° C. By the two last methods the film of copper is exceedingly thin, and such coppered goods can only be treated in certain bronzing solutions, as those of a strongly corrosive nature easily dissolve the copper and produce a very patchy appearance on the surface of the article. Copper nitrate solution, for example, is such a liquid, and for a coppered brass article to receive a good colour the deposit of copper must be thicker than can be obtained by simple immersion processes, *i.e.* it must be deposited by means of an electric current, when any desired thickness of copper can be obtained.

Buchner states that a pale copper colour can be imparted to brass by heating it over a clear charcoal fire, free from smoke, till it assumes a blackish-brown colour, then immersing it in a solution of zinc chloride, and allowing it to boil gently, finally well swilling the article in clean water. The operation requires repetition.

A golden-yellow colour is imparted to brass by dipping it in a very dilute neutral solution of copper acetate, which must not contain any trace of free acid, and kept at a medium temperature for a few seconds. A golden-yellow to orange colour may be imparted by immersing polished brass wares in a mixture of 50 grains of caustic soda, 500 grains of water, and 100 grains of copper carbonate. The shades of colour appear in a few minutes. When the right tint is obtained, wash well with water and dry in saw-dust.

A dark yellow is produced on brass by immersing it for five minutes in a saturated solution of common salt containing some free hydrochloric acid, and in which mixture as much ammonium sulphide has been dissolved as the liquid is capable of taking up.

§ 140. Dr. Kayser states that an ordinary gold colour may be imparted to brass in the following manner:— Dissolve 150 grains of sodium thiosulphate in 300 grains water, and add 100 grains of antimony chloride solution. Boil for some time, filter off the red-coloured precipitate, well wash with water, transfer the precipitate to a vessel containing 4 pints of hot water, add a saturated solution of sodium hydrate, and heat till the precipitate is dissolved. Immerse the brass articles in this solution till the desired shade of colour is reached. If they remain in it too long they will become gray.

§ 141. Dr. Schwarz states that a colour from yellow to brown may be obtained on brass as follows:—Dissolve 50 grains of lead acetate in $\frac{1}{2}$ pint of water, and add a solution of sodium hydrate until the precipitate which first forms is redissolved, then add 150 grains of red potassium ferricyanide. When the whole is in solution immerse the brass goods at the ordinary temperature, when they assume a golden-yellow colour. By warming the solution to 40° or 50° C. the yellow colour changes to brown.

§ 142. Dittrich recommends the following method for obtaining a gold colour on brass. Prepare a solution of

3000 grains distilled water.
30 ,, sodium thiosulphate.
10 ,, lead acetate.

The articles are first covered with silver in a silver-plating

bath, then immersed in the bronzing solution raised to a temperature of 60° to 70° C. The metal assumes a golden-yellow colour after two or three minutes, due to the formation of silver sulphide. The articles are then swilled in water and dried out in sawdust.

§ 143. The following solutions are given to show the effects of chlorides on brass in producing colours of a shade varying from brown to greenish-drab :—

Copper chloride	1 part.
Water	1½ parts.

A brass ash-tray assumed an olive-green drab colour which, after exposure to daylight, became very dark chocolate with evidence of decomposition on the edges, showing a copper-coloured border, which is probably anhydrous cuprous chloride. A brass casting also became olive-green drab in colour after immersion. The results are tabulated as follows—

(*a*) Brass tray (stamped) . . .	olive-green drab.
(*b*) ,, ,, . . .	reddish-brown.
(*c*) Brass (casting)	olive-green drab.

When (*a*) was heated on the stove it became salmon-coloured, and after scratch-brushing was found to be well coated with copper ; (*b*) was heated on a hot iron plate till it became nut-brown, and then lacquered. This nut-brown appears to deliquesce and to rub off under the finger unless it is lacquered whilst hot. It darkens on exposure to sunlight.

A series of quantitative experiments were performed to determine whether the coloration and subsequent coppering were due to a true deposition, or to a corrosion of the surface with consequent loss of zinc. These experiments

are recorded in § 75, and proved in each case that there was a loss in weight of copper. It should be stated that the coppering reaction appears only to occur during the heating stage of the process, for if the work is scratch-brushed without being previously heated, the colour is rubbed off and the underlying brass is exposed. The presence of chlorine also appears to be essential to the success of the process, for salts of copper other than the chloride fail to give the coppering reaction, but any other soluble copper salt may be used successfully, provided that a small amount of some other soluble chloride is also added.

The blackening effect on copper, which has already been referred to when dealing with the bronzing of that metal in copper chloride, is much more rapid and deeper in tone than with brass under the same circumstances.

§ 144. Similar colours to those produced on brass in copper chloride may be obtained when ferric chloride is also added. The following solution was used :—

Copper chloride	500 grains.
Ferric chloride	500 ,,
Water	20 ounces.

Time of Immersion.	Temperature.	Remarks.
2 minutes	15° C.	Colour of coinage, bronze.
3 ,,	,,	,, ,, ,,
4 ,,	,,	,, ,, ,,
1 ,,	70° C.	Do., but paler in tone.
5 ,,	80° C.	,, ,, ,,

The colour may be deepened by adding a very small quantity of a soluble sulphide to the above solution.

Scratch-brushing removes the colour almost completely, although the effect is improved by the scratch-brush if the articles are subsequently re-immersed in the solution, then well swilled and dried out in sawdust. The brown colour became a dark olive-green on exposure to daylight. Another solution of double the strength of the first one did not have any great advantage except to yield a slightly darker tone of colour.

This solution works better at a moderate temperature than it does at the boiling-point. A brass ash-tray bronzed in this solution, and after swilling and drying out in sawdust, was placed upon a hot plate, when it assumed a salmon-red colour similar to that produced on copper when bronzed in the same solution. On scratch-brushing, a perfect coating of copper was found upon the surface of the tray.

This tray weighed before bronzing . . .	14·6098 grams.
,, after heating and scratch-brushing .	14·5713 ,,
Loss =	·0385

Ferric chloride freely dissolves copper when hot, but in the case of brass, the zinc is probably dissolved more readily than the copper. It should, however, be remembered, as stated on a previous page, that the coppering reaction does not occur during the immersion of the work in the bronzing solution, but during the subsequent heating, therefore it must be due to a decomposition of the surface compound deposited during the immersion.

A solution of ferric chloride alone was then tried, using the following proportions :—

Ferric chloride	1 part.
Water	4 parts.

(*a*) Brass ash-tray . .	dull and crystalline brass.
(*b*) ,, ,, . .	good coppered surface.

This solution alone appears to be of little value, but as the liquid dissolves copper, the solution after a time becomes impregnated with copper chloride, and then acts as in the preceding method. The tray (*a*) was not bronzed at all. The tray (*b*) was done after the solution had been experimented with for some time on copper articles, and of course had dissolved a considerable amount of copper. The coppering effect was produced by pickling and subsequent heating.

§ 145. Experiments were performed with a mixture of copper sulphate and ferric chloride, using the following proportions :—

Copper sulphate (saturated solution)	16 ounces.
Ferric chloride	$\frac{1}{4}$ ounce.
Water	$\frac{3}{4}$,,

(*a*) Brass ash-tray	slaty-green.
(*b*) ,, ,, after pickling and heating	copper surface.
(*c*) Cast brass-plate	slate colour.
(*d*) Brass ash-tray	purple-brown.

(*a*) and (*c*) were not sensibly altered on exposure to daylight ; (*b*) had a surface of pale medal brown bronze, which deliquesced on exposure to air, and washed off completely in water, leaving a nice dead surface ; (*d*) was pickled and heated to produce a coppered surface, and then re-pickled, when it assumed a purple-brown colour, which turned black on exposure to light.

§ 146. A peculiar bronzing effect on brass, which may be useful in certain cases, is obtained with a solution of

Copper sulphate	1 ounce.
Common salt	1 ,,
Water	4 ounces.

(*a*) Brass ash-tray	white, inclining to drab.
(*b*) Cast brass	greenish-gray.

(*a*) when scratch-brushed after bronzing showed an unaltered brass surface. When heated on a hot plate after bronzing it became medal brown in colour, and on continuing the heat metallic copper appeared on the surface, varnished with a glaze which deliquesced on exposure to air. This deposit gave a slightly acid reaction. Brass pickled in the copper sulphate solution alone, without the addition of common salt, did not give the copper colour reaction, which confirms the idea that the reaction is due to the presence of chlorine. The white bronze of (*a*) is partly removed by drying in sawdust, but if the article is gently dried and lacquered with zapon the coating is preserved for some time, but ultimately turns green.

§ 147. Wuttig recommends the following ingredients as a means of producing the ordinary antique bronze (green). He states that the pickle produces in a very short time a durable coating of oxide. The cream of tartar may be replaced by vinegar, and the copper salt omitted in the second or third repetitions after the metal has been once stained. The following solution was tested by us for colouring brass :—

Ammonium chloride	8 grains.
Cream of tartar (pure)	24 ,,
Common salt	48 ,,
Copper nitrate	1 ounce.
Water	5 fluid ounces.

(*a*)	Brass ash-tray	olive-green.
(*b*)	,, ,, ...	nut-brown.
(*c*)	,, ,, ...	well coppered.

(*a*) was simply pickled in the solution, swilled, and dried out in sawdust; (*b*) and (*c*) were each pickled like (*a*), then put on the hot stove and heated until the olive-green colour disappeared, and was succeeded by a rich medal red colour; (*c*) was finally scratch-brushed.

§ 148. The combined effect of copper acetate and ammonium chloride on brass was tested with the following results. Copper acetate alone appears to have very little action on brass unless concentrated, and the mixture of acetate and ammonium chloride acts very slowly. This solution is reputed to have been used at the Paris Mint for bronzing medals. Some bronzers also add red iron oxide, which is held in suspension.

Copper acetate	200 grains.
Iron oxide	200 ,,
Ammonium chloride . . .	70 ,,
Water	20 fluid ounces.

(*a*)	Brass tray . . .	yellowish-brown.
(*b*)	,, . . .	brown ochre.
(*c*)	,, . . .	bronze coinage colour.

(*a*) was simply immersed in the hot solution, swilled, and dried out in sawdust; (*b*) and (*c*) were each pickled in the hot solution, swilled, dried, and heated on a lacquering stove for ten minutes. Both acquired the same brown ochre colour; (*c*) was then severely scratch-brushed without destroying the whole of the colour produced by heating. They do not appear to alter by exposure to diffused daylight.

The solution was then varied by using sixteen ounces of water and four ounces of vinegar to the other substances above-mentioned.

(*a*)	Brass ash-tray . . .	yellowish-brown.
(*b*)	,, ,, ...	dark brown ochre.
(*c*)	,, ,, ...	,, ,,

(*a*) was pickled as before; (*b*) was pickled and heated as above; (*c*) was scratch-brushed after heating.

§ 149. A solution composed of copper sulphate and copper chloride dissolved in water may be employed for bronzing brass and copper, but the slate colour produced darkens considerably on exposure to daylight, so that the method cannot be recommended.

Copper sulphate	400 grains.
Copper chloride	400 ,,
Water	1 fluid ounce.

Brass articles were pickled in the hot solution, swilled and dried out in sawdust when they were coloured as above. On heating them on a hot plate the colour became darker.

Similar results were obtained by using the following solution :—

Copper chloride	300 grains.
Ammonium chloride . . .	200 ,,
Water	5 fluid ounces.

§ 150. A good brownish-drab colour may be obtained on brass by means of a mixture of

Copper sulphate	1 part.
Zinc chloride	1 ,,
Water	2 parts.

The mixture is smeared over the work, which is then heated till it is dry. Or more water may be used to form a solution, in which the work may be immersed. The colour does not appear to change much by exposure to light. By heating the bronzed brass article on a hot stove in the usual way the surface is coppered.

§ 151. Walcker recommends the following ingredients for producing a brown colour on copper. It may be used to produce a yellowish-green colour on brass.

The proportions given below were employed in our experiments—

Ammonium carbonate . . .	300 grains.
Copper sulphate	150 ,,
Vinegar	5¼ fluid ounces.

The whole was evaporated to dryness, and to the residue was added

Vinegar	5¼ fluid ounces.
Oxalic acid	4 grains.
Ammonium chloride . . .	1½ ,,

The above was then boiled and the insoluble portion filtered off. The article, if too large to be immersed in the solution, should be well warmed and the solution painted on uniformly with a brush. Boiling water is then poured over to wash it and to hasten the drying. When dry the article is rubbed with an oiled pad, and lastly with a dry pad.

(*a*) Brass ash-tray . . .	oiled and wiped dry.
(*b*) ,, ,, . . .	dried in sawdust only.

Immersion was found to be much better than rubbing or painting on the solution. Wiping with an oiled pad

removed some of the bronze, unless it was done very gently.

The colour produced on (*a*) and (*b*) was distinctly yellowish-green, but the bronze does not appear to change by exposure to daylight.

The insoluble portion, from which the liquid used in the above experiments was filtered off, was next rubbed into a thin paste with a few drops of the above-mentioned solution, and then rubbed on some fresh articles, which were heated on a hot plate after swilling and drying. When dry the paste was well washed off with water.

(*c*) Brass ash-tray	yellowish-green.
(*d*) Coppered ash-tray . . .	deep brown.

Neither of them was quite uniform, but that was doubtless owing to the operation being only performed once. We infer from our experiments that the method is suitable for large work that cannot be immersed.

§ 152. The following solutions have been recommended as bronzing liquids, but no useful results could be obtained by their use in our experiments. The hot solutions, as one would naturally expect, dissolved both copper and brass rapidly.

Copper nitrate	1 ounce
Hydrochloric acid . . .	5 ounces

(*a*).

Copper nitrate	½ ounce
Copper chloride	½ ounce
Hydrochloric acid . . .	4 ounces

(*b*).

The work is recommended to be pickled in solution (*a*), then immersed in the solution (*b*).

(1)	Brass ash-tray,	solution used cold	.	pale brassy bronze.
(2)	,,	,,	(*a*) only, cold	,, ,,
(3)	,,	,,	(*b*) only, cold	,, ,,
(4)	,,	,,	(*a*) and (*b*), hot	,, ,,
(5)	,,	,,	(*a*) only, hot .	,, ,,
(6)	,,	,,	(*b*) only, hot .	,, ,,

§ 153. A solution, which is capable of yielding useful colours, may be employed with the ingredients in the following proportions :—

Copper chloride	½ ounce.
Water	¾ ,,
Tartaric acid	75 grains.
Sodium hydrate	¼ ounce.
Water	10 ounces.

The tartaric acid is used to prevent precipitation of the copper by the sodium hydrate, and to this is added the sodium hydrate solution.

(*a*) Brass ash-tray . . .	pale umber-brown, with light bluish-green sheen.
(*b*) ,, ,, . . .	pale umber-brown.

The tray (*a*) was pickled in the hot solution, swilled in hot water, and dried out in sawdust; (*b*) was pickled, heated, and quenched in the hot solution, then scratch-brushed and re-pickled. Brass in this solution passes through various shades of colour—gold, deep gold, umber-brown, nickel-yellow, then brass reappears.

§ 154. The following solution has been recommended, and it certainly does produce a very good dark green colour on brass, but unfortunately this turns to a deep black on exposure to daylight :—

Copper acetate	50 grains.
,, sulphate	200 ,,
Common salt	70 ,,
Acetic acid solution	4 ounces (1 acid to 16 water).
Water	50 ounces.

A solution similar to the above is said to be used by the Japanese for bronzing copper and its alloys. It suffers from the same defect as the former solution with regard to light changes, but in a much less degree as regards brass.

Copper acetate	100 grains.
,, sulphate	500 ,,
Common salt	180 ,,
Saltpetre	100 ,,
Water	10 pints.

(*a*) Brass ash-tray	greenish-drab.
(*b*) ,, ,,	olive-green drab.
(*c*) Cast brass	,, ,,

The tray (*b*) was immersed for a longer time than (*a*). The plate (*c*) was of a reddish-drab on the embossed parts, and olive-green drab on the groundwork.

§ 155. The effect of platinum chloride on brass is different to that of most other chlorides in that it produces a gray to black colour as shown in the following results. Two solutions were used, both very dilute, but one was double the strength of the other :—

(*a*) Platinum chloride solution, containing ·2 per cent of platinum chloride and 99·8 per cent of water.

(*b*) Platinum chloride solution, containing ·4 per cent of platinum chloride and 99·6 per cent of water.

The brass must be scrupulously clean and uniformly polished on the plain parts. The metal was kept in the weaker solution until it received a stain, then it was transferred to the stronger solution. The deposit is largely removed in scratch-brushing and the surface rendered paler in colour.

As this is a case of platinating by simple immersion one would only expect the difference between the deposit on brass and copper to be one of degree. If the work is left too long in the solution the deposit becomes powdery and is easily rubbed off. Heating the work after bronzing does not appear to improve it.

A very strong solution of platinum chloride, containing 5 per cent, gave the following results :—

Articles of brass were made warm, and the solution was applied to their surfaces by means of a paint-brush. The result in each case was a dark gray colour.

On evaporating the aqueous solution, which probably contained some free acid, to dryness, and redissolving the residue in alcohol, the following results by immersion were obtained :—

(*a*) Brass tray . . .	a coating of reguline platinum.
(*b*) ,, . . .	black deposit.

It appears that if a black colour is required it is best to use an alcoholic solution. The tray (*a*) was scratch-brushed after bronzing ; (*b*) was swilled and dried out in sawdust. The deposit of platinum seems more firmly adherent to brass than to copper.

BLACK COLOUR ON BRASS

§ 156. Elsner states that the production of a good black colour on brass and bronze has excited a considerable amount of attention, and many attempts have been made to secure a good durable colour. It is in great demand for colouring telescope tubes and similar optical instruments. He says: "We have many times been consulted concerning this matter, and for that reason have made some experiments with the following results:—

"To impart a black bronze to brass we make use of the following substances:—An acid solution of pure silver, by dissolving pure silver in pure nitric acid; or a solution of bismuth nitrate; or of nitric acid alone; or an acid solution of silver nitrate containing some copper nitrate (such may be obtained by dissolving an ordinary silver coin in nitric acid); or a solution of copper nitrate alone may be used.

"According as one or the other of the above substances is used so the bronzed article will vary in tone. With copper nitrate it is always very black; the bismuth solution gives a particularly deep brown colour; that of copper and silver a deep black.

"In every case the bronzed brass acquires a deeper shade, when the brass after bronzing is placed for some time in a solution of liver of sulphur, antimony sulphide, or in a solution of freshly prepared sulphuretted hydrogen, or exposed to a moist atmosphere containing that gas.

"The operation is very simple, and is executed in the following manner:—

"The respective metals are dissolved in pure nitric acid, taking care to have the acid in excess. Solution readily takes places without having recourse to the application of artificial heat. The solution is then applied to the previously heated articles by means of a paint-brush, and the heating of the metal is continued till the surface is quite dry. The solution employed must not be too concentrated, otherwise the coloured film will wear off under the action of the brush or rubber in finishing. It is better to dilute the solution considerably with soft water before applying it to the object, as the thinner the layer of liquid the firmer will the bronze adhere to the metal.

"Immediately the bronzing liquid has evaporated from the surface of the metal, it is rubbed with a dry leather or brushed with a dry brush in order to produce uniformity of surface. If nitric acid alone is used to colour the brass, it forms on the surface a layer of copper nitrate, and there is therefore no need to previously dissolve copper in nitric acid for this purpose.

"The operation may require to be repeated several times, and a little experience will make known the most convenient method of manipulation.

"If the colour is required to be an intense black, the brass should be treated with the saline solution of liver of sulphur before mentioned. In about half an hour the surface will become a deep black, and the operation is completed by rubbing the surface with a dry leather.

"When the operation has to be repeated several times with the solution in question, it is necessary that the last should be very concentrated, otherwise the free acid will dissolve the bronze already formed. The bronzed surface

should be covered with a solution of ammonium sulphide, taking care that the bronze is equally affected. It is not necessary to cover it with an excess of the sulphide because the brass easily takes a black colour in a little time by the liberation of sulphuretted hydrogen. If it is desired to favour the disengagement of this gas a few drops of hydrochloric acid may be added to the ammonium sulphide, so that the brass is plunged into a medium charged with sulphuretted hydrogen.

"Another method for achieving the same result may be employed by using a solution of one part of neutral tin chloride, and two parts of gold chloride, which must not be too dilute. The two liquids are mixed, and then used for bronzing the brass. In about ten minutes the article is wiped with a damp linen rag. If the use of a large excess of free acid has been avoided the surface is a dead black, and very durable."

§ 157. In order to test the effectiveness of certain reagents referred to in the preceding paragraph, and to discover a good permanent black bronze the following experiments were performed :—

Potassium sulphide	30 grains.
Ammonium chloride	90 ,,
Water	2 pints.

The solution was applied with a brush, when the brass articles were allowed to stand about an hour and then were scratch-brushed. The operations were repeated until a satisfactory colour was obtained. Other experiments were performed by immersing some brass articles in the solution instead of painting the solution on the work.

(*a*) Brass tray	. . . .	tarnished to coppery-red.
(*b*) ,,	. . . .	light brown colour (poor).

(*a*) was done by painting the solution on to it as described above; (*b*) was bronzed by immersion in the hot solution which was found to be much more effective, especially for copper goods.

This solution reacts very slowly on brass and cannot be recommended as a bronzing liquid for that metal, as much better results can be achieved by other solutions. A much lighter tone is imparted by means of scratch-brushing. The solution soon becomes exhausted and requires renewal. When freshly prepared and warm, the solution smells like ammonium sulphide, but after working some time it smells like water containing flowers of sulphur in suspension.

The same solution, but with different proportions containing larger quantities of the two salts with the same quantity of water as before, was found to produce a darker shade of colour. The following proportions were used :—

Potassium sulphide . . .	15 grains.
Ammonium chloride . . .	200 ,,
Water	5 fluid ounces.

A solution of ammonium sulphide was found to give results identical with those of potassium sulphide.

§ 158. The following complicated method of preparing a solution has been recommended, but was found by the author to be quite unnecessary, as identical results can be obtained by potassium sulphide and water, as referred to above, without the use of the other ingredients :—

Cream of tartar	60 grains.
Copper acetate	60 ,,
Water	2 fluid ounces.

The solution obtained is then to be treated with liquid ammonia until the precipitate first formed redissolves. Then

Potassium sulphide . .	120 grains,
Ammonia	3 fluid drachms,
Water	1¼ ,, ounces,

are added to the above. This mixture is not suitable for brass, but it acts instantaneously on copper.

§ 159. The following recipe for bronzing may be classed in the same category as the preceding, but in addition to it containing unnecessary and expensive constituents, they are positively damaging to the metal and serve no useful purpose :—

Mercury chloride . . .	150 grains.
Ammonium nitrate . . .	150 ,,
Water	4 fluid ounces.

Ammonia, till the precipitate redissolves.

After the work has been pickled in the above solution, it is to be immersed in a dilute solution of ammonium or potassium sulphide.

The object of the mercury chloride is evidently to impart a coating of metallic mercury to the metal, as both copper and brass are almost instantly coated with mercury when immersed in the first solution.

A brass ash-tray dipped in the two solutions successively and scratch-brushed was observed to be simply amalgamated. The dark colour may be made permanent by omitting the scratch-brushing, and simply drying out

in sawdust. The effect on brass is as useless as in the preceding methods.

§ 160. The following is another instance of a bronzing liquid containing unnecessary constituents :—

Mercury sulphide	.	50 grains.
Potassium sulphide	.	50 ,,
Sodium hydrate .	.	1 fluid ounce (20 % solution).
Water . .	.	3 ,, ounces.

A brass tray immersed in this solution assumed a dark brown colour with a patchy appearance. This result was only obtained with difficulty, and a second attempt to procure a similar result completely failed. From this it may be inferred that a bronzing effect can only be produced on brass by this method when the solution is just freshly prepared, and even then the colour is very poor.

Results equally as good can be obtained by omitting the mercury sulphide and sodium hydrate, as the potassium sulphide is the only effective reagent.

§ 161. The following solution of potassium sulph-antimoniate is recommended by Böttger for copper :—

A solution for testing this method was made by dissolving 100 grains of potassium sulphide in 12 fluid ounces of water and then saturating the hot solution with freshly precipitated antimony sulphide. The following results were obtained :—

(*a*) Brass tray .	.	.	rich shellac-brown.	
(*b*) ,,	.	.	,,	,, but paler.

This solution acts on brass very slowly. (*a*) was produced after fifteen to twenty minutes' immersion; (*b*) occupied about half an hour. (*a*) was done in the freshly pre-

pared solution; (*b*) was done after several other articles had been bronzed. Both were scratch-brushed at intervals. Copper takes a brown to black colour very quickly in this solution, the shade of colour depending on the length of the immersion.

§ 162. The following solution acts much more quickly on brass than the preceding one, producing a dark gray deposit of metallic arsenic, which becomes lighter on scratch-brushing:—

White arsenic oxide . . .	1 ounce.
Hydrochloric acid . . .	2 fluid ounces.
Sulphuric acid	½ ,, ounce.
Water	12 ,, ounces.

§ 163. A very good black colour can be obtained on brass, as previously explained, by a solution of

Copper nitrate	50 parts.
Water	100 ,,

If the work is too large for immersion, it is heated and the solution is applied by means of a paint-brush, when the heating is continued until the surface is dry. It is then gently rubbed with a linen pad, and brushed with or immersed in a solution of

Potassium sulphide	10 parts.
Water	100 ,,
Hydrochloric acid	5 ,,

Immersion of the work in the liquid produces much better results, and, after draining off the superfluous liquid, it is heated on a hot plate or over a clear fire till dry. We have obtained more uniform results by using a solution about three times more dilute than the preceding solution of copper nitrate, viz.—

Copper nitrate	100 parts.
Water	600 ,,

The heating process must not be continued longer than is necessary to convert the whole of the green salt which forms on drying into the black copper oxide.

A good black can be thus produced on brass in this way without recourse to the second pickling in potassium sulphide, but this second pickling is probably advantageous in fixing the colour.

§ 164. The following bronzing liquid is due to Böttger :—

Mercury chloride	100 grains.
Antimony chloride . . .	100 ,,
Water	20 fluid ounces.

The above salts are dissolved in the water and a current of sulphuretted hydrogen passed through until the whole of the mercury and antimony are precipitated as sulphides. The precipitates are allowed to settle, when the supernatant liquid is poured off and the precipitates washed several times with water; they are then boiled in a 20 per cent solution of sodium hydrate until they are completely dissolved.

One hundred grains of a solution of sodium thiosulphate are then added to the dissolved sulphides and the whole allowed to stand till the liquid is clear. The clear solution is then decanted off, heated, and the work immersed in it. Or the solution may be painted on to the hot work in the usual way—

(*a*) Brass tray	slaty-black.
(*b*) Coppered tray	,,

There is apparently no difference in the reaction of this solution on brass and to that on copper.

The colour produced is probably due to a deposit (by simple immersion) of antimony, the deposit being rendered darker by the presence of a sulphide in the solution. If the work is smooth and bright, the black deposit will be correspondingly smooth and bright, but if the work has a dead or dull appearance then the deposit will be correspondingly dull.

The appearance of the articles after bronzing may be improved by lightly scratch-brushing, which operation, when judiciously done, gives a better finish to the work without sensibly diminishing the intensity of the colour. The same remarks also apply to the final polishing with a calico mop and rouge. The work may be rendered grayer by heating it after bronzing, but the colour obtained is not so rich as before.

With regard to this solution it should be stated that the mercury compound is quite unnecessary and useless, as the bronzing is quite as effective without it. Moreover, mercury sulphide is insoluble in sodium hydrate, so that in reality the mercury compound is thrown away and only the antimony compound used.

This was proved by the following experiment :—

Antimony sulphide . . .	100 grains.
Sodium hydrate	350 ,,
Water	4 fluid ounces.

The mixture was boiled for some minutes, the undissolved portion allowed to settle, and the liquid used for bronzing. The results were precisely similar to those recorded above.

One hundred grains of sodium thiosulphate were added,

and an article immersed in it, with precisely the same result; therefore the only effective bronzing agent is the solution of antimony sulphide in the caustic soda.

When the work which has been bronzed in either of these solutions is scratch-brushed, the deposit is that of slightly violet-tinted antimony.

§ 165. Another method of producing a black colour on small brass articles is recommended by Buchner, as follows—

Copper carbonate	10 parts.
Liquid ammonia	70 ,,
Water	150 ,,

The article is to be rubbed with the solution until it blackens, when it is heated over a hot coal-fire (without putting it in the fire). After cooling it should be rubbed with olive oil.

We tested the method in the following way :—

Copper sulphate	250 grains.
Water	6 ounces.
Sodium carbonate	300 grains.

The action of the sodium carbonate is to precipitate the copper as carbonate, which is allowed to settle, and the supernatant liquid filtered off. The residue is well washed, just sufficient liquid ammonia added to redissolve it, and the liquid diluted to one pint.

The articles were then immersed in the solution and heated over a clear flame. After several immersions and subsequent heatings the brass assumed a reddish-black colour, and a copper article similarly treated became dead black.

All these ammoniacal copper solutions, when heated, deposit a black substance on the bottom of the vessel containing the bronzing solution, ammonia being expelled. This black substance is soluble both in ammonia and in nitric acid. We have used this solution largely for parcel bronzing, and it is probable that this deposit is the cause of the black colour we obtained on brass.

The filtrate obtained from the precipitated copper carbonate was also tested as to its power of bronzing brass, which received a light yellowish-drab colour on immersing it in the hot solution.

The colour on the copper article which was made black in the present bronzing liquid is anomalous, as we failed to reproduce it. It was thought that the solution was too impoverished to give the effect as it had been in use for some time, so a new solution was made, and the experiments repeated with a coppered tray, but the result was not a permanent black as before. Although we succeeded in getting the tray black all over, the coating would not withstand brushing with a soft brush without exposing the copper. This method, as described above, is of little use for bronzing copper.

§ 166. The following method, which is a modification of the former one, and which taught us the cause of the varied results previously obtained, is one of the best with which we are acquainted for giving a rich, firm, durable coating to brass. The only precaution required is to avoid excess of ammonia which practically dissolves all bronzes produced by means of copper solutions.

Copper nitrate	10 ounces.
Water	20 ounces.
Ammonia solution	...

The copper nitrate is dissolved in the water, and the ammonia cautiously added, until the precipitate which forms at first is just redissolved. It is probable that the black deposit is due to copper oxide. The following results were obtained :—

(*a*) Brass ash-tray . . .	black (lustrous).
(*b*) ,, ,, . . .	steely-black.
(*c*) Coppered ash-tray . . .	crimson.
(*d*) Part coppered, part brass .	black and crimson.

(*a*) was swilled after bronzing and dried out in sawdust; (*b*) was heated after drying out; (*c*) and (*d*) were not heated; (*d*) became black on the brass parts, and a crimson-coloured bronze on the coppered parts.

The solution becomes very turbid after a time, and in this condition appears to yield the best results. It reacts very quickly on brass, producing a magnificent dark blue-black colour, which is firmly adherent, and is capable of taking a good polish.

On somewhat strongly heating the articles after bronzing the dark blue changes to a steely-black, which is not so rich in colour as before heating.

The bronzing reaction does not take place till the solution is warm, and goes on rapidly when the solution is worked hot. The bottom of the dish in which the bronzing was done was covered with a deposit, which was partly black and partly reddish-brown.

The only effect produced on copper by the solution was a transparent crimson coloration. It was thought that, as the presence of zinc in the brass enabled the solution to be decomposed, with the formation of the black coating before mentioned, the copper might be also blackened by

immersing it in the hot solution in contact with zinc, but no such change could be effected in this way. The crimson colour on copper makes a very effective contrast with the blue-black on brass for parcel bronzing.

A black colour may be obtained by dipping the work in the clear solution (which for this purpose may contain an excess of ammonia) and heating on a hot plate, or over a clear fire until the black colour appears. This plan, however, is much more tedious, involves more labour, and yields an inferior result.

§ 167. It may be desired, previous to the operation of bronzing, to impart a brass surface to copper articles so as to enable them to take a black colour by one of the methods referred to in the preceding paragraphs. Or, on the other hand, to give a copper surface to a portion of a brass article, with the object of getting a contrast in the colours and so produce a most artistic effect.

For the purposes of coppering, a solution of copper sulphate, with the aid of an electric current, is most generally employed. This salt is low in price and easily obtainable. It is also very valuable on account of its electrical relations with regard to different metals, by which copper is deposited in a practically pure state, even from impure solutions.

Copper may also be deposited on brass by simple immersion. If the copper article is surrounded by iron wire and suspended in a dilute solution of copper sulphate or copper nitrate, it soon becomes coated with a firmly adherent, but very thin, coating of copper.

A surface coating of bronze may be given to copper goods by immersing them in a boiling solution of cream of tartar containing tin. A half-hour's boiling will be

sufficient for tinning, especially if a few drops of tin chloride are added to the solution. When the coating is sufficiently thick, the objects are rinsed in hot water and dried; they are then heated moderately until they have taken a bronze colour.

For brassing copper, the preceding solution is replaced by a saturated solution of ammonium chloride, containing some granulated zinc, in which the copper articles are boiled as before. When the zincing is completed the article is rinsed in hot water, dried, and heated as with bronze until the brass colour appears. To accelerate the zincing, a little zinc chloride may be added to the bath.

If, after heating, the articles appear iridescent or patchy in places, these irregularities may be removed by polishing with tripoli and scratch-brushing.

The change which occurs in this method may be easily understood. By the boiling with tin or zinc respectively a coating of one of these metals is obtained on the surface of the copper, and on heating unites with the copper, forming a surface alloy, even by the aid of a very moderate temperature.

§ 168. In a previous paragraph it was explained that a very beautiful black could be obtained by means of a solution of copper nitrate neutralised by ammonia. The same result may be obtained by the following:—

Copper sulphate	400 grains.
Water	½ pint.
Liquid ammonia	...

The copper sulphate is dissolved in the water, and sufficient ammonia added to just redissolve the precipitate which first forms. Brass pickled in the cold solution

acquires an asphaltum brown colour which easily rubs of. Brass pickled in the hot solution gives an adherent deposit of the same colour as above.

A stronger solution than the above-mentioned one was then tried, viz.—

Copper sulphate . .	2 ounces.
Water	just sufficient to dissolve the copper sulphate.
Ammonia . . .	to neutralise and make slightly alkaline.

A brass tray immersed in this solution, made hot, was almost immediately turned a beautiful and permanent blue-black colour. As copper assumes a beautiful Florentine tint in this solution, brass articles, which have been parcel coppered and then bronzed in the above solution, present a very beautiful contrast in the copper and brass parts respectively.

§ 169. The following is one of those complicated mixtures which are often met with in books dealing with workshop receipts, and used by bronzers who often treasure them as profound secrets known only to themselves. It need only be stated here that a simpler mixture is not only cheaper but yields better results :—

Hydrochloric acid . . .	20 fluid ounces.
Copper sulphate . . .	1½ ounces.
White arsenic	1½ ,,
Copper acetate	160 grains.
Iron sulphate	160 ,,
Ammonium chloride . . .	80 ,,

A series of experiments with the above solution gave a steely-gray colour to brass, but the coating withstood scratch-brushing very imperfectly.

One hundred grains of sodium thiosulphate was then

added to the solution, and brass articles immersed in it received a darker shade of colour than before; the coloured film was more firmly adherent to the metal, and better withstood the action of the scratch-brush. Warming the work previous to the immersion favoured the formation of the colour, but two or three immersions and subsequent scratch-brushings were necessary to get a good effect. Warming the solution does not appear to make much difference.

BROWN COLOURS ON BRASS

§ 170. For some years, writes the Bavarian, Industrial, and Trade Paper in 1886, "beautifully coloured bronze figures, which rapidly won the public favour, have been brought into the market by the French. The models for them were chiefly executed by French sculptors, and then cast in brass or bronze. The colouring produced on these figures is of great variety and taste, according to their character, which greatly adds to their beauty and popularity. The bronzing varies from all shades of faint or clay-yellow to reddish-brown, and red to dark brown and black. It has a good bronze appearance and adheres firmly to the metal, that is—it chemically unites with it.

"A firm in Philadelphia, which was engaged in the fabrication of art-metal wares, but not of such figures as above described, received from one of its customers two uncoloured figures, with the request to colour them similar to the French bronzing. After trying different recipes, the idea was suggested of making use of sulphur combinations of arsenic and antimony, which was carried out as follows—

"The articles are thoroughly cleaned and rinsed in

water until every trace of acid is removed, for if any acid is left in the pores or crevices it comes out after bronzing, and produces ugly black spots and streaks, which it is impossible to properly remove. The solution is applied to the article by means of a pad of cotton-wool or a thick soft brush. It is best to commence by putting on a dilute solution of ammonium sulphide as thinly as possible, and quickly go over certain limited parts of the surface. The quicker and the more equally this is done, the better will be the final effect. It is then allowed to dry, and any separated sulphur, etc., brushed off. A dilute solution of arsenic sulphide, dissolved in ammonia, is now applied, which produces a colour similar to that of Mosaic gold. Another coating of the same solution is given when the former one is dry, and so on until the desired tint is obtained. The more of this liquid there is used the darker will be the colour. And it is possible to get a very dark brown.

"A reddish-brown colour is obtained by means of a solution of antimony sulphide in ammonium sulphide, and one is able to produce the most delicate pink and the deepest dark red colour. By rubbing some parts more than others a high metallic lustre is obtained.

"It should be remembered that ammonium sulphide and ammonia dissolve the colouring matter again, so that if any badly-coloured parts appear they may be dissolved off and the colouring repeated. In such a case it is generally preferable to remove the whole colour from the figure and commence again. Just as the solutions of antimony and arsenic can be dissolved in ammonia or ammonium sulphide, so can the same be dissolved in potassium or sodium hydrate or sulphide, and sometimes the latter are the more useful.

"If the figure is pickled dead instead of bright, then the tone of the bronzing will be different. When the metal is left too long in the acid it assumes a greenish-gray surface, which should be rubbed with a cloth until it shines and a good lustre appears on the metal. This surface takes a dead yellow colour by treatment with the above-mentioned metallic sulphides. The article should not be warmed for bronzing."

§ 171. A beautiful brown colour, known as Bronze Barbédienne is produced, according to Langbein, in the following way :—

"Freshly precipitated arsenic sulphide and antimony sulphide are digested with ammonium sulphide solution until they are nearly dissolved and just a faint muddiness remains. The solution is raised to a temperature of 35° C. and the brass-ware immersed in it. The colour is at first a golden-yellow, then brown, when it should be removed and well scratch-brushed in order to bring out the colour, then on re-immersion in the bath the articles take the desired tone. The operations may require repeating several times in some cases. If, after using several times, the solution fails to work satisfactorily some more antimony sulphide solution is added. As this solution decomposes on standing it is made fresh each time it is required for use.

"By this method only solid brass articles can be coloured brown; to brassed zinc and iron articles the solution imparts brownish-black tones, which however are very beautiful. Upon brass, as well as upon zinc and iron coated with brass, Bronze Barbédienne may be produced as follows :—Mix 3 parts of red antimony sulphide with 1 part of finely powdered red iron oxide, and triturate the mixture with ammonium sulphide so as to form a thin

paste. Apply the mixture to the object by means of a brush, and after allowing it to dry in a drying chamber, remove the powder by brushing with a soft brush."

§ 172. Various shades of colour may be produced on brass by means of a solution of barium sulphide, but the action is slow unless the solution is strong and used hot. With a hot solution containing 100 grains of barium sulphide to 1 pint of water an umber-brown colour, with a rich blue sheen, can be obtained after a few minutes' immersion. The first effect produced upon brass is a gold colour, this is succeeded by an iridescent crimson, passing to the brown colour mentioned above.

Brass, which has been parcel coppered and then bronzed in this solution, looks very well provided that the copper predominates.

§ 173. **Smoke-bronze.**—Bronzing with smoke is sometimes resorted to in order to give the metal an ancient appearance. This is effected by exposing the work to the smoke of a fire for some days, when it receives a firm coating of a dark colour. The articles are generally suspended over the smoky fire of a furnace by means of brass wire. When the furnace is sufficiently heated the smoke is maintained by burning hay and other substances which produce copious smoke with the coal. When the right tint is attained they are removed from the furnace and allowed to cool without touching them with the hands. The hotter the articles have been made the darker will be the colour. If the articles which have been smoked have been previously coated with a green bronze, then it is well to finish with a waxed brush.

§ 174. A useful solution for colouring brass may be made by dissolving copper sulphate in water—

Copper sulphate	8 ounces.
Water	1 pint.

(*a*) Brass ash-tray . . .	pale umber-brown.
(*b*) ,, ,, . . .	light coinage bronze.

The brass trays bronzed in this solution lost weight by the process, probably due to the solution of the zinc and oxidation of the copper. A copper tray bronzed in the same solution gained in weight.

While copper bronzes very slowly in this solution, brass readily takes a colour, especially if it is scratch-brushed after a short immersion in the solution, and then re-immersed. The tray (*a*) was heated on the lacquering stove after bronzing, when it lost its umber-brown colour and assumed the appearance of a light coinage bronze similar to (*b*), which was bronzed after the solution had been in use for some time.

In another series of experiments with common copper sulphate employed in the same proportions as above, the brass assumed a slaty-brown colour. As the same quality of brass was employed in both cases, it is presumed that the difference was due to impurities in the solution. The tray first turned red, and on scratch-brushing assumed a nickel-yellow colour, then on re-immersion became slaty-brown.

§ 175. The above experiments were varied by using basic copper sulphate mixed with sufficient water to form a paste.

Preparation of the mixture—

(*a*) Precipitate copper oxide from 1000 grains of copper sulphate by caustic potash.
(*b*) Mix the precipitate with 1000 grains of copper sulphate.
(*c*) Mix (*b*) with sufficient water to form a thin paste.

The work was then covered with the paste, and heated over a charcoal fire. The process was repeated once. The residue left on the work was difficult to remove and the surface was not uniformly coloured.

A brass ash-tray was pickled in the above mixture after diluting with water to form a solution, when the tray assumed a light slate-green colour.

§ 176. Another variation of the copper sulphate solution was tried in the following way :—

Copper sulphate solution . . .	600 grains.
Water	2 pints.

The above solution was boiled and rendered neutral by the addition of a solution of sodium hydrate, then 1500 grains of red iron oxide were added.

The work was immersed in the above liquid, taken out, and heated. The operations were repeated until a brown tone was secured. This solution gave very good results on copper and brass by immersion only, and the colour was darkened by the subsequent heating. The effects by heating the work over a charcoal fire were better than by heating over a gas-flame.

The experiments were repeated with a solution as above, but omitting the iron oxide. The colours were similar, but paler in tone. Brass articles received a light brown, with a bluish-green sheen.

§ 177. The following mixture is recommended by one bronzer, but we failed to obtain any good results either on copper or brass, even when the work was left in the solution for a long period of time :—

Copper sulphate solution .	½ pint (1 of salt to 4 of water).

Tartaric acid solution . .	10 fluid ounces (100 grains of acid per ounce).
Sodium hydrate solution . .	12 fluid ounces (1 of alkali to 5 of water).
(*a*) Coppered ash-tray . . .	brassy colour.
(*b*) Brass ash-tray	nickel-yellow colour.

The above was then tried with a slight excess of ammonia added, when the following results were obtained :—

(*a*) Brass ash-tray	pale greenish-brown.
(*b*) „ „	very dark brown.
(*c*) Brass casting	light brown.

The solution worked very slowly and cannot be recommended. Doubtless the discordant results were due to the action of ammonia.

§ 178. The following solution containing copper acetate in addition to copper sulphate yields much better and quicker results on copper than on brass :—

Copper sulphate	1 ounce.
„ acetate	2 ounces.
Water	1 gallon.

A brass ash-tray received after a short time a light umber-brown colour, with bluish sheen, while a cast brass article assumed a coinage bronze colour only after a considerable time. The great disadvantage of solutions containing acetic acid is the iridescence which it gives to the bronzed surface. The first change observed in this as in many other solutions is a slight tarnishing. If the work is then rinsed in water, scratch-brushed, and re-immersed in the solution the tarnishing goes on much more rapidly and uniformly than at first, and this second tarnishing is quickly succeeded by the colour which the solution is

intended to impart to the metal. Contact with zinc accelerates the preliminary tarnishing.

The above solution may be varied by the addition of potassium nitrate, when brass receives a paler bronze colour than in the preceding solution.

§ 179. Another solution similar to the preceding one is valuable for copper and gives a light colour to brass.

Copper acetate . . .	112 grains.
,, sulphate . . .	540 ,,
Vinegar	160 fluid grains.
Water	20 ,, ounces.
(*a*) Brass ash-tray . .	light umber-brown, with green sheen.
(*b*) Cast brass article .	greenish-yellow on the raised parts, and the same, but redder on the groundwork.

A brass ash-tray heated on the lacquering stove after bronzing became paler in colour, passed through a nickel-yellow tint, then darkened, and became somewhat like antimony, but inclining to purple.

§ 180. The effect of copper nitrate, neutralised by ammonia, in producing a black bronze, has been referred to in a previous part; but brown colours can also be obtained by its agency, with the aid of suitable mixtures and careful manipulation. Several shades, varying from nickel-yellow to jet-black, are capable of production by its means. The following are some of the results after numerous experiments :—

A saturated solution of copper nitrate was used—

(*a*) Brass ash-tray	slaty-brown.
(*b*) ,, ,, ...	black.
(*c*) Brass casting	dark Indian red.

(*a*) was immersed in the hot solution and received the colour

mentioned above, which became darker with a longer immersion; (*b*) was bronzed by immersion the same as (*a*), and then heated on a hot iron plate. The process was repeated two or three times with alternate scratch-brushings.

Dilute solutions of copper nitrate produce merely a stain on brass and copper work immersed in them. A black bronze cannot be produced by pickling in copper nitrate alone, it is necessary to heat the work afterwards without rinsing in water. If the work is placed on a hot plate and covered with an inverted glass beaker, the following changes will be observed:—The work dries of a light green colour, and brown fumes are given off. After a little time the green colour changes to black by the decomposition of the nitrate and the formation of black copper oxide, which assumes a brighter and more uniform appearance by brushing with a waxed brush. The copper casting (*c*) treated in a similar way assumed a dark Indian red colour on the deep parts and groundwork, while the more prominent parts became black.

§ 181. The following mixture containing copper nitrate was tested as a bronzing agent:—

Copper nitrate	1 ounce.
Tartaric acid	½ ,,
Sodium hydrate . . .	½ ,,
Water	8 fluid ounces.

No useful effect could be obtained by immersing brass or copper in this solution. Four fluid drachms of ammonia were then added, with the result that a brass tray was bronzed a very dark brown. From this it may be inferred that the addition of tartaric acid and sodium hydrate is unnecessary, as the same effect may be produced by copper nitrate and ammonia alone.

§ 182. A solution of copper nitrate of various strengths, with sodium hydrate added until a slight precipitate just begins to form, gave the following results on stamped brass :—

1. A 20 per cent copper nitrate solution . . greenish-brown.
2. A 10 ,, ,, ,, . . ,,
3. A 15 ,, ,, ,, . . ,,

It was impossible to say from the observed action that one was better than the other.

§ 183. The following mixture may be useful in certain cases, as a fairly good bronze was obtained on brass :—

1. Copper nitrate, 20 per cent solution, 3 fluid ounces.
   Copper acetate, saturated ,, ,,

A brass tray received a neutral greenish-brown colour.

2. Copper nitrate, 20 per cent solution, 3 fluid ounces.
   Copper acetate, saturated ,, 6 ,,

A brass tray received a coppery yellowish-green.

3. Copper nitrate, 20 per cent solution, 1 fluid ounce.
   Copper acetate, saturated ,, 4 ,, ounces.

A brass tray was bronzed a similar colour to that done in the first solution.

§ 184. A method which is somewhat widely used for producing on brass different shades of colour, varying from blue to brown, and from a blue-black to dead-black, is conducted in the following way :—To a solution of a soluble copper salt, such as the sulphate, is added a solution of sodium carbonate, which precipitates the copper as copper carbonate. This is allowed to settle, and the supernatant liquid filtered off. The precipitate is well washed, and dissolved in ammonia solution to form the bronzing solution.

Copper sulphate	600 grains.
Water	1 pint.

The sodium carbonate solution consists of two parts water and one part of the crystallised salt. The colour obtained will, to a large extent, depend on the condition of the solution, *i.e.* on the quantity of ammonia added. The best results are obtained when a slight trace of the precipitate remains undissolved, because then the operator knows that the ammonia is not in excess. The following results were obtained with a warm solution :—

(*a*) Brass tray, just immersed, taken out, and swilled . . .	brownish-black.
(*b*) Brass tray, immersed longer than (*a*),	deep brownish-black.
(*c*) ,, ,, (*b*),	black.
(*d*) ,, ,, (*c*),	light umber.
(*e*) ,, immersed a considerable time,	dead brown.

This is one of the most valuable solutions for brass that we have worked with, every shade of colour is beautiful. The tray (*d*) showed an exceedingly beautiful lustrous brown colour.

§ 185. An extraordinary series of different colours from the same solution may be obtained on brass by using a solution of lead acetate containing some sodium thiosulphate. The following table shows the results obtained by the author on a series of brass plates :—

Sodium thiosulphate	200 grains.
Lead acetate	200 ,,
Water	1 pint.

Metal.	Time of Immersion.	Temperature of Solution.	Remarks.	Colour.
Brass	5 sec.	87° C.	...	Pale gold
,,	10 ,,	,,	...	Deeper gold
,,	15 ,,	,,	...	Brown gold
,,	20 ,,	,,	Not uniform	,,
,,	25 ,,	,,	...	Crimson
,,	30 ,,	,,	...	Purple
,,	35 ,,	,,	Blue on edge	,,
,,	40 ,,	,,	Blue extended	,,
,,	45 ,,	,,	Iridescent	Bluish - crimson-green
			...	
,,	50 ,,	,,	Pale blue edge	Mottled bronze centre
,,	55 ,,	,,	Do., and iridescent	Mottled bronze centre
,,	1 min.	,,	...	Pale blue
,,	65 sec.	89° C.	...	Mottled purple
,,	70 ,,	,,	...	Less mottled than above
			...	
,,	75 ,,	,,	Pale blue on edge	Pinkish-bronze
,,	80 ,,	,,	Bluish sheen	Nickel colour
,,	85 ,,	,,	Mottled	Blue and pink
,,	90 ,,	,,	Pink centre	Very pale blue
,,	100 ,,	,,	Pink diminished	,,
,,	110 ,,	,,	Mottled	Purple and yellow
,,	120 ,,	,,	,,	Bluish-yellow and pink
			...	
,,	2½ min.	,,		Pale purple
,,	3 ,,	,,	Yellowish on edge	Bronze centre
,,	4 ,,	87° C.	Mottled	Pink and yellow
,,	5 ,,	,,	,,	Pink and gray
,,	10 ,,	,,	...	Pink and pale blue

§ 186. A series of experiments were made with a solution in which sulphuric acid was substituted for lead acetate.

Sodium thiosulphate	200 grains.
Sulphuric acid	¼ ounce.
Water	20 ounces.

A variety of colours was obtained on brass but of very inferior quality as compared with the former solution.

BRONZING AND COLOURING OF ZINC

§ 187. The metal zinc is known in commerce under two different names—zinc and spelter, the latter appellation being applied to the metal when in the cast state. It is then highly crystalline, with a bluish shade. On rolling the metal into sheets this crystalline structure is largely destroyed. The metal, when exposed to moist air, takes up oxygen, forming a gray film of sub-oxide, and afterwards forms basic zinc carbonate by the action of carbonic acid. This grayish-white deposit is of little artistic value, and is not worth imitating by chemical means, as is the case with copper and its alloys, so that the colouring of zinc for ornamental purposes is entirely artificial, no natural patina being used as a model or as a standard for imitation. Zinc compounds are chiefly white in colour, such as the oxide, sulphide, carbonate, and chloride. These white compounds turn to a dirty gray colour when exposed to ordinary atmospheric influences.

One of the most valuable properties of zinc is its power of taking the finest impressions of a mould into which it is poured, and it is one of the very best metals for fine castings, and, as already stated, the cast metal can be coated with copper, brass, and other metals with great facility, and these deposits can be made to receive many

of the various bronze shades of solid copper, brass, etc. The use of zinc for cast and wrought work has spread very rapidly, and a new branch of industry has become firmly established, almost rivalling in bulk and importance that of brass. With regard to the rolled form of the metal, the modern discovery that it could be rendered malleable by working it at a temperature of about 100° to 150° C. has greatly extended its usefulness and stimulated its application for many purposes. It is true that zinc coated with brass or copper is not equal in all cases as a base for bronzing to that of the solid metals themselves, but in many others it is equally good, especially when a good firm deposit has been secured.

§ 188. **Black Colour on Zinc.**—Zinc articles often require to be coloured black so as to imitate the beautiful dark shades which lend such a charm to brass and copper goods. There are many solutions in which a black deposit is formed on zinc by simple immersion, but several of these deposits are unfortunately non-adherent, and, in nearly all cases, it is necessary to repeat the operation several times, with alternate heating, to get a firmly adherent coating. In this category may be classed certain salts of copper, to which an excess of ammonia has been added; or the insoluble salts of copper, such as the hydrate and carbonate which have been dissolved in an excess of potassium tartrate.

There are many difficulties in the way of producing a good durable black coating on zinc, equal to that formed on brass for philosophical instruments, such as mountings for miscroscopes, and other optical apparatus, so as to absorb the light and prevent reflection. The black for such a purpose must be a true bronze and not merely a

coating of paint or varnish, which would not attain the object in view. The bronze must be uniformly distributed over the surface and perfectly adherent. It must also be quite opaque and as free as possible from lustre.

In order to obtain a uniform result the manner of conducting the operation, the temperature, the purity, the strength, and composition of the solution must not vary. Many failures result from inattention to these details, and many different recipes have been given from time to time in consequence of this. Many operatives recommend the use of salts of silver added to the bronzing bath to yield a more intense black colour, and some recommend the addition of gold. In all cases it must be borne in mind that zinc exerts a considerable reducing action on solutions which are unaffected by copper and brass, and this leads to the necessity of exercising great caution in operating with it. If, for example, zinc which has been bronzed in a solution containing copper nitrate is heated over a fire, as in the analogous process for brass, the copper will be reduced to the metallic state, and gives to the surface an appearance far from that of a good bronze colour.

§ 189. Dullo recommends a solution of antimony chloride in alcohol for producing a black colour.

Antimony chloride . . .	200 grains.
Alcohol	4 fluid ounces.
Hydrochloric acid . . .	2 ,, drachms.

Zinc blackens in this solution, and the work, after allowing to dry by exposure to air, or by igniting the alcohol, requires to have oil or varnish applied to fix the colour, or it will rub off. The deposit of antimony in this case being

in a powdery state makes it impossible to apply this method for producing a firmly adherent patina.

Brass, when immersed in this solution in contact with zinc, becomes coated with antimony.

Tin is darkened in colour by immersion, but the deposit easily rubs off. The deposit does not dry after varnishing.

Iron is unaltered by dipping in the solution.

Lead and iron are blackened by immersion in contact with zinc, but only at the points of contact.

All the above effects produced by zinc contact are impracticable on a commercial scale.

§ 190. Knafft states that a firmly adherent black coating may be given to articles of rolled and cast zinc by means of a solution of the double sulphate of nickel and ammonia. The method was tested by means of the ordinary nickel-plating solution diluted with water. No deposit was obtained upon zinc, brass, tin, iron, or lead.

Sulphuric acid in small quantity was then added to the above solution and the liquid gently heated, when zinc on immersion received an adherent dark purplish-gray colour. Tin was stained by immersion in contact with zinc. Iron appeared to be unaffected. The deposit was rendered much paler by scratch-brushing.

§ 191. Kletzinski states that a solution of molybdic acid, or ammonium molybdate in nitric acid, made very dilute, furnishes a good liquid for producing a brown patina on cast zinc. The object assumes iridescent colours on immersion which he considers to be due to molybdenum oxide. The following proportions were tried with the following results:—

Ammonium molybdate . .	100 grammes.
Ammonia	150 cubic centimetres.
Water	½ litre.

In English measures this equals—

Ammonium molybdate . .	1550 grains.
Ammonia	2325 ,,
Water	1 pint.

Zinc acquired a beautiful iridescent appearance after a few minutes' immersion in the solution. On continuing the process the iridescent colours were succeeded by a light yellowish-brown colour, and this, on warming the solution, was followed by a slaty-black which was more opaque than any of the preceding colours.

Brass and tin are unaffected when immersed alone, but tin when placed in contact with zinc assumes a beautiful dark violet colour which is firmly adherent to the metal. Iron in contact with tin is simply stained.

§ 192. Puscher states that the following method gives a good black colour on zinc :—

Copper sulphate	30 parts.
Potassium chloride . . .	30 ,,
Water	400 ,,

If any iron oxide is present it will remain undissolved and should be filtered off. The perfectly cleaned zinc goods are then immersed in the clear solution at the ordinary temperature till a deep black deposit is formed, when they are removed, washed, and dried. The coating is firm and will stand rubbing with a cloth. In the case of large articles they should be painted with the solution or moistened with a sponge. Should the articles show copper-brown spots, then the parts should be again moistened with the solution till the proper black colour is attained. By rubbing, the surface assumes an indigo colour, with bright lustre. By brushing with linseed oil or wax the colour becomes a deep lustrous black. The dry blackened zinc

article may be immersed in a solution of Syrian asphalt dissolved in benzol, and then rubbed with a woollen cloth.

The following solution was tried :—

Copper sulphate, saturated solution . .	1 part.
Potassium chloride ,, . .	1 ,,
Water	2 parts.

The work was dipped momentarily in the solution, for if it is left in only a few seconds, the black deposit which forms on the surface will swill off when rinsed in water. It is better not to swill, but to drain off the solution and put the work on a hot plate until just dry. The process must then be repeated until a satisfactory colour is obtained. The colour we obtained on both rolled and cast zinc was a grayish-black. Zinc is coppered in a dilute solution.

§ 193. Sainte-Claire Deville has shown that the transformation of manganese nitrate into peroxide is effected at a temperature of 200° to 250° C. Ph. Neumann has taken advantage of this reaction to produce a black colour on zinc. Manganese nitrate may be put in contact with zinc without any notable change taking place, but when heated the salt undergoes the change mentioned above. Now zinc requires a temperature of 415° C. to melt it, so that the temperature at which the nitrate is decomposed and the metal blackened does not affect the zinc as regards fusion.

He states that "the method is applicable to small and large goods either by immersion or by painting with a brush. After coating them with the solution they should be left to dry very slowly over a charcoal fire, or, in the case of small articles, over the flame of a spirit-lamp. In

this way a more uniform and a more intense black colour is obtained. After each application of the solution and drying, the work must be scratch-brushed. When the proper colour is obtained (which may be only after seven or eight repetitions) it should be rubbed with the smallest quantity of linseed oil to give it a good finish.

"Should the nitrate not be available, the black oxide may be dissolved in hydrochloric acid, then precipitated as carbonate with sodium carbonate, and the latter just dissolved in nitric acid. The solution is then evaporated to a syrupy consistence and allowed to stand for the nitrate to crystallise out.

"The black colour adheres firmly to the zinc, which can be bent or even hammered without it chipping off. It is also able to resist the action of the atmosphere, in consequence of its chemical nature, even better than the black copper oxide formed on brass."

In consequence of the above method being so strongly recommended we spent a considerable amount of time in testing it with the following solutions :—

I.	Manganese nitrate, saturated solution	½ fluid ounce.
	Water	4 ,, ounces.
II.	Manganese nitrate, saturated solution	¼ fluid ounce.
	Water	4 ,, ounces.

For the first immersion the stronger solution was used, and for the repetitions the weaker solution was employed. The zinc articles were taken out of the solution and dried gradually on a hot iron plate to the required temperature. After drying they assumed a reddish-brown colour, and on heating to a still higher temperature they became gray and finally a blackish-gray. The black colour was not dense

enough for a useful bronze. The solution is better suited to cast than to rolled zinc.

Sheet-steel takes a fairly good colour in this solution. From the experiments recorded above we consider the method to be but an inferior one, as other solutions have yielded much better results with much less time and trouble. We cannot endorse the opinion expressed by Neumann as to its valuable properties. We have tried solutions varying in strength from 1 in 20 up to a completely saturated solution, and heated the zinc articles from about 200° C. up to nearly the melting-point of zinc, without obtaining thoroughly satisfactory results.

§ 194. A good black having a brownish tint can be formed on zinc goods by immersing them in a solution of copper nitrate of the following strength :—

Copper nitrate	1 ounce.
Water	5 fluid ounces.

A good black colour is produced almost immediately by immersing zinc in this solution. The brownish tint referred to above is probably due to the deposit containing finely precipitated copper. Immediately after pickling the work may be rinsed in clean water, and dried out in sawdust.

§ 195. A grayish-black colour can be obtained on zinc by immersion in a solution of

Copper acetate	250 grains.
Ammonium chloride . . .	250 ,,
Water	5 fluid ounces.

On immersing the article in the solution a black deposit forms almost immediately on the surface, which looks very rich and lustrous after swilling in water, but it is

not adherent and easily rubs off, leaving a brown coloration on the surface of the metal. If the article is previously dipped in liquid gum and then immersed in the solution, swilled, and dried gently on a hot plate, the coating becomes much darker, and may afterwards be vigorously brushed without removing the grayish-black coating. By repeating the process several times a fairly good black deposit may be obtained.

§ 196. Böttger recommends the following solution for imparting a black colour to zinc :—

Platinum chloride . . .	40 grains.
Gum Arabic	40 ,,
Water	1 fluid ounce.

We have tested the above solution in various ways, both of the strength given and in different degrees of dilution, but the result is always a black patchy coloration, which on scratch-brushing reveals a deposit of reguline platinum. With very dilute solutions the colour is more gray than black, and inclining to purple in places, which may be largely removed by brushing. The colour produced by platinum chloride is likely to be more permanent than those obtained by copper salts, but it is generally less dense in appearance.

§ 197. **Brown Colour on Zinc.**—A reddish-brown colour is produced on zinc articles by means of the following solution :—

Copper chloride	1 part.
Water	4 parts.
Ammonium chloride, saturated solution .	5 ,,

On pickling zinc in this solution a black deposit is formed, which is easily rubbed off.

If the pickled zinc is dried on a hot stove, the black coating is decomposed with the formation of a reddish-brown coating, which is improved by brushing. The heating process must not be continued longer than is necessary to produce the brown colour, for if heated much beyond that stage the coating will also rub off completely.

§ 198. A firmly adherent dark brown colour can be obtained on zinc by immersion in the following solution :—

Copper sulphate	50 grains.
Sugar	75 ,,
Sodium carbonate . . .	500 ,,
Water	4 ounces.

§ 199. **Gray Coating on Zinc.**—An excellent coating of arsenic on zinc, giving its surface a gray colour, may be obtained by means of the following solution :—

Arsenious oxide	100 grains.
Sodium phosphate . . .	36 ,,
Potassium cyanide . . .	100 ,,
Water	5 fluid ounces.

The work must be first rendered perfectly clean and then immersed in the cold solution. If too large for immersion the liquid may be painted on to the article by means of a brush.

§ 200. Puscher gives the following solutions for producing a green patina on zinc goods :—

(*a*)	Copper nitrate solution . .	5 fluid ounces (1 of salt to 100 of water).
(*b*)	Ammonium carbonate . .	50 grains.
	Water	5 fluid ounces.

The work is recommended to be dipped first in (*a*), then in (*b*) and set aside to dry.

In testing the above method a black deposit was obtained after immersion in solution (*a*), which was unaltered by dipping in solution (*b*). After allowing it to stand twenty-four hours no change was observed, except the formation of a grayish-white film, probably of ammonium carbonate.

The solution (*a*) was tried of various strengths from 1 to 20 per cent, but with the formation only of a black deposit in each case. There was no indication of a green patina.

§ 201. **Different Colours on Zinc.**—Böttger has obtained a variety of colours on zinc, which should contain as little as possible of lead, by means of the following solution :—

Copper tartrate . . .	300 grains.
Sodium hydrate . . .	400 ,,
Water	10 fluid ounces.

It is quite necessary for success in this process that the zinc articles should be scrupulously clean.

When immersed in the solution the metal first becomes coated with a film of copper, and then assumes after a minute or two colour films in the following order :— Yellow, light brown, brown, crimson, blue, purple, very pale purple, light sea-green, then light crimson again.

All these colours are iridescent, and are evidently due to thin films. It is difficult to get any one of them uniformly distributed over the surface of the article. There are generally two or more colours present on a small area of surface, and they are always very beautiful.

A hot solution works very rapidly, and is more difficult to be controlled than a cold solution.

Continued immersion in the hot solution for five to ten

minutes produces a dense gray deposit, with a slightly reddish tint.

§ 202. Similar results to those mentioned in the preceding paragraph may be obtained by the following solution, which is due to Ludersdorff:—

Copper sulphate	100	grains.
Cream of tartar	100	,,
Sodium carbonate	750	,,
Water	8	fluid ounces.

This solution behaves much in the same way as the preceding one; the colours, however, are more dense, but less brilliant, and distribute themselves over the surface after the same manner as the mottled designs commonly produced on the edges of books.

The colours are produced in both hot and cold solutions, and are preceded by the deposition of a film of copper. All the colours of the spectrum appear to be present at any one time, so that it is impossible to produce a single colour alone on the surface.

PARCEL COPPERING AND BRONZING AS APPLIED TO FINE ZINC CASTINGS

§ 203. After thoroughly cleaning the zinc work in the usual way, a stout coating of brass should be deposited in the hot cyanide brassing solution by means of an electric current, after which it should be well swilled in water and dried out in hot sawdust.

After removing the loose sawdust, all those parts which are not to be coppered should be carefully painted over with copal varnish of good quality by means of a camel-hair pencil. A little asphaltum varnish may be

added to the copal varnish in order to render it darker in colour than the brass, so that the operator may see every stroke he makes with the pencil he uses in the process. The work must now be allowed to remain for a few hours in a warm place to dry.

When the varnish is dry, the work is suspended in an electro-depositing bath of copper cyanide until a sufficient coating of copper is obtained.

It should then be well rinsed in water, dried, and soaked in turpentine and brushed until the varnish is removed and the underlying brass is exposed. It is then well rinsed in hot potash solution, and finally in plenty of water, when it is ready for bronzing.

A good liquid to employ in this case is a hot solution of copper nitrate. The article is immersed for a little while, then removed, swilled in water and well scratch-brushed to give a good and uniform surface, then re-immersed in the bronzing bath, and the operation repeated if necessary.

The colour obtained upon the brass by this method is a very dark green (nearly black), and upon the copper a light nut-brown or bronzed flesh tint.

If the casting is a figure subject, it is best after brassing all over to stop off all the draped parts and deposit copper on the face and all the naked parts. The hair, sandals, etc., may also be stopped off with advantage, but the taste and judgment of the operator will generally dictate the most effective treatment in this respect.

Of course several of the other solutions mentioned in the section on bronzing of copper and brass may be employed, but the one recommended above is very effective, and the two colours blend together very harmoniously.

Brass, copper, or other metals may be treated in a

similar way to the above. In the case of a brass article, the electro-brassing would of course be omitted. It is very important in the case of zinc, or any metal that has to be both brassed and coppered, that the brassing should be done first, and not *vice versa*, as the free ammonia in the brassing solution dissolves the copal varnish.

BRONZING AND COLOURING OF IRON AND STEEL

§ 204. Iron in the pure state is not a commercial article, and therefore the effect of various agents in producing colours on its surface need not be considered here ; but iron in the condition of wrought or malleable iron, steel, and cast iron is of very great importance, and will therefore claim our attention from their industrial value.

Wrought iron is almost silver-white in colour, but rapidly tarnishes when exposed to moist air at the ordinary temperature, and still more rapidly oxidises when heated under the same influence. Steel is bluish-white when soft, but becomes much whiter when hardened. When it contains much carbon it is close-grained and lustrous. Many elements when alloyed with it, such as chromium, make it still whiter and more brilliant. Cast iron is grayish-white in colour, varying with the condition in which the carbon exists, as well as with the amount and nature of the impurities present.

Iron and steel become coated with two distinct grades of colour by oxidation, according to the kind of oxide which is produced. The red oxide is generally formed by a slow process of oxidation, and varies in tone from brown to a bright red colour, containing iron and oxygen in the proportion of two atoms of iron to three atoms of oxygen.

The black oxide contains three atoms of iron to four atoms of oxygen, and is generally produced when iron is strongly heated in contact with air or oxygen. Various shades of colour may therefore be produced by a combination of these two chief oxides.

Iron forms a brassy-looking compound with sulphur when the proportion of atoms of iron to atoms of sulphur is as one is to two, or as three is to four. When the proportion is as one is to one, then the colour varies from a bronze to black, depending upon the physical condition of the compound.

These various shades may be produced by means of various solutions, or by heating in contact with gases or vapours. A still greater variety of shades may be induced by taking advantage of electro-deposition, as explained under the heading of Electro-Chemical Metal-Colouring. In addition to the colours obtained by the processes referred to above, there is also the method of obtaining rainbow tints by the deposition of exceedingly thin transparent films of oxides or other compounds which produce an optical effect, as in the case of the well-known process of tempering steel. The surface of the iron or steel is made bright, and the article gradually heated. When the temperature reaches 220° C., a faint yellow colour appears; this is succeeded by other colours as the process proceeds. The following table shows the temper used for various articles, the lowest temperature indicating the hardest temper :—

Temperature.	*Colour.*	*Article.*
220° C.	Faint yellow.	Surgical instruments.
230° ,,	Straw yellow.	Razors.
255° ,,	Brownish yellow.	Scissors, chisels, etc.
265° ,,	Purplish brown.	Axes, planes, etc.

Temperature.	*Colour.*	*Article.*
277° C.	Purple.	Table-knives.
288° ,,	Light blue.	Swords, springs.
293° ,,	Dark blue.	Fine saws.
316° ,,	Blackish-blue.	Hand-saws.

In order to obtain the above colours with certainty, various alloys, whose melting-points are known, are used. Messrs. Parkes and Martin have proposed the following as suitable for this purpose :—

Lead.	Tin.	Melting-point.
14	8	214° C.
15	8	221° ,,
16	8	228° ,,
17	8	240° ,,
28	8	257° ,,
36	8	262° ,,
60	8	275° ,,
96	8	284° ,,
100	8	289° ,,

§ 205. **Gray Colour on Iron.**—A good and uniform dark gray colour can be imparted to iron and steel by first depositing a coating of copper on the articles and then immersing in the following solution :—

Ammonium sulphide solution . .	1 fluid ounce.
Water	6 fluid ounces.

It will be well to repeat the immersion once or twice to get a good colour. The deposit will withstand scratch-brushing. Potassium or sodium sulphide may be used in the place of ammonium sulphide.

§ 206. A light gray colour may be imparted to iron

and steel by means of a solution of antimony chloride. The articles are first coppered as in the previous method, then immersed in the following solution :—

Antimony chloride . .	30 grains.
Water	1½ fluid ounces.
Hydrochloric acid . .	to make the solution clear.

A deposit of antimony may be obtained on plain steel without the previous coppering, but it has a very poor appearance as compared with the method recommended above.

§ 207. A good gray colour can be obtained on iron and steel by immersion in a hot solution of

Arsenious oxide . .	50 grains.
Hydrochloric acid .	sufficient to dissolve the above.
Water	1 fluid ounce.

No effect is produced upon either plain or coppered steel in a cold solution.

§ 208. **Blue Colour on Iron.**—A blue colour is said to be obtained on iron and steel by the following method :—

Clean the articles free from all dirt and grease, then immerse in vinegar, well wipe off and dry. Now moisten them with hydrochloric acid by means of a cloth, allow to dry, and place in sand in a sand-bath until the desired blue colour is obtained. We could not succeed in getting a uniform colour by this method. Probably if the metal had been polished very bright a better result might have been obtained.

§ 209. The following method of producing a blue colour on iron and steel is due to Böttger :—

Potassium ferrocyanide . . .	25 grains.
Ferric chloride	25 ,,
Water.	20 fluid ounces.

We were unable to get any coloration on steel in this solution even after eighteen hours' immersion. Immersion in the solution, and drying on hot plate without rinsing in water, was tried without any useful effect.

§ 210. Puscher has produced a variety of colours on iron and steel by means of a mixture of lead acetate and sodium thiosulphate. The following proportions were tried, with the results enumerated below, the colours altering with the time of immersion :—

Lead acetate	50 grains.
Sodium thiosulphate	50 ,,
Water.	5 fluid ounces.

The solution must be used hot.

1. Light brown colour.
2. Darker ,,
3. Purple and blue mixed.
4. ,, ,, but paler tone.
5. Beautiful uniform light blue colour.
6. Steel-gray.
7. Black colour, after half an hour's immersion.

In order to produce a uniform colour all over, the article must be completely immersed, so as to be equally heated.

§ 211. **Black Colour on Iron.**—A bluish-black colour may be obtained on iron and steel by means of a solution of sodium thiosulphate.

Sodium thiosulphate . . .	50 grains.
Water	5 fluid ounces.

The bluish-black colour produced by this solution has a somewhat warm coppery tint. The effect was produced by pickling in the hot solution during about ten minutes, with scratch-brushing at intervals. Two scratch-brushings were found to be sufficient. No advantage was obtained

from using a stronger solution, viz. 100 grains of the thiosulphate to 5 fluid ounces of water.

§ 212. A solution for producing a dead-black colour on iron and steel, which is said to give good results, is as follows :—

Bismuth chloride	1 part.
Mercury chloride	2 parts.
Copper chloride	1 part.
Hydrochloric acid	6 parts.
Water	50 ,,

The solution is recommended to be applied to the work by means of a brush, the liquid allowed to dry on, and the work boiled for half an hour in water. The operation is repeated until the proper colour is obtained. The colour is said to be fixed and improved by immersing during a few minutes in a bath of boiling oil, then removing and heating until the oil is driven off.

We could only obtain a zinc-gray colour by this method after three repetitions, and even this colour was unsatisfactory.

§ 213. Meriteus states that a bright black colour can be obtained on iron by making it the anode in distilled water, kept at 70° C., and using an iron plate as a cathode. The method was tested as follows—

A piece of bright sheet pen steel was placed in distilled water and made the anode by connecting with the positive pole of a plating dynamo, and a similar sheet was connected with the negative pole to form the cathode. An E.M.F. of about 8 volts was employed. After some time a dark stain was produced, but wanting in uniformity.

The experiment was repeated with larger plates, when a good blue-black colour was obtained on the anode in

half an hour. On drying out in sawdust the colour appeared less dense, and inclined to a dark straw tint. The back of the plate was also coloured, but not regularly. The face of the cathode was discoloured with a grayish stain on the side opposite to the anode, but on the other side the appearance was almost identical with the back of the anode. The water became of a yellowish colour.

Fresh distilled water was then boiled for a long time so as to expel all trace of the oxygen absorbed from the atmosphere, and the experiment repeated as in the former cases. No perceptible change took place after the connection had been made with the dynamo for a quarter of an hour. After the interval of one hour a slight darkening occurred, but the effect was much less than that produced in five minutes in aerated water.

The action of the liquid in colouring the steel is evidently one of oxidation, due to the dissolved oxygen, which becomes more chemically active under the influence of the electric condition, and gradually unites with the iron.

§ 214. The following solution for producing a dark colour on iron and steel has been recommended :—

Ferric chloride	10 parts.
Water	200 ,,
Potassium sulphide	1 part.

The articles may be immersed in the solution or painted with it, then allowed to dry by exposure to the air, and finally brushed with a waxed brush. A fairly good black bronze may be obtained in this way.

The above solution, with the omission of the potassium sulphide, may be used for bronzing iron or steel. The colour is brown after two immersions with subsequent air-drying, and uniformly distributed over the surface.

A dense and fairly uniform grayish-black colour can be produced on iron by digesting flowers of sulphur with turpentine, painting the work with the liquid, allowing to dry, and then heating over a clear fire, or on a hot stove.

BRONZE COLOUR ON IRON

§ 215. A bronze-like colour is produced on iron and steel goods by exposing them to the vapours of heated aqua regia, then dipping them in melted vaseline, and heating until the vaseline begins to decompose.

This process yields a nice warm brown bronze colour on iron and steel.

The steel articles, in our experiments, were heated by holding them over a smokeless flame without bringing them in contact with it. The excess of vaseline was shaken off, and the process completed by holding the article for a very short time in the flame itself. The work was afterwards wiped with a soft cloth, but if it is rubbed too hard some of the coating is removed.

§ 216. Iron and steel goods, such as gun-barrels, for example, may be bronzed a brown colour by means of a paste of antimony chloride. It is used for bronzing mixed to the consistence of cream with olive oil, and is known in the trade as "bronzing salt." The iron is slightly heated, covered evenly over its surface with this mixture, then left until the requisite colour is obtained. The paste may be made more active by adding a little nitric acid.

§ 217. Another method of producing a brown colour on iron and steel may be employed by using a mixture of—

Nitric acid	½ ounce.
Spirits of nitre	½ ,,
Alcohol	1 ,,
Copper sulphate	2 ounces.
Ferric chloride	½ ounce.
Water	2 pints.

Dissolve the copper sulphate in water and then add the other ingredients. In the case of gun-barrels the burnishing and marking is effected by means of the burnisher and scratch-brush. The polishing is effected by rubbing with a piece of smooth hard wood, called polishing wood. They are then varnished with shellac varnish, or with lacquer, and finally polished with hard wood as before.

Instead of the above mixture, the following may be used :—

Copper sulphate	1 ounce.
Spirits of nitre	1 ,,
Water	20 ounces

In any case the iron must be previously well cleaned and rendered quite bright; it is then freed from grease by rubbing with whiting and water, or with quicklime and water. The bronzing mixture is then put on and allowed to remain twenty-four hours, when it is brushed off with a stiff brush. If the article is not sufficiently deep in colour the operation is repeated once or twice.

§ 218. The following method is said by Buchner to be suitable for bronzing gun-barrels :—

Ferric chloride	400 grains
Antimony chloride	10 ,,
Gallic acid	10 ,,
Water	5 fluid ounces.

We found that iron and steel acquired in this solution, when used hot, first a very pale blue tint, then on longer immersion a darker colour, passing into a purple. After a still longer immersion the purple was succeeded by a plumbago-gray colour. The deposit is evidently due to antimony.

No immediate effect is obtained in a cold solution.

§ 219. Iron and steel articles may be bronzed by decomposing certain organic compounds on their surface by means of heat, with the formation of a deposit of a mixture of ferric and magnetic oxides. If, for example, the surface of an iron article is coated with a layer of linseed oil, and the whole is heated over a fire, hydrocarbons are eliminated which assist in colouring the metal. With regard to bodies which cannot be conveniently heated in this way, a uniform coating of oxide may be imparted by plunging them in water at a temperature of 80° to 100° C.

According to Hess, iron articles may also be bronzed by immersing them in an acid solution of ferric chloride, and allowing them to remain in it for some time. The water of the solution is decomposed, and the liberated oxygen unites with the iron, forming a dark layer of oxide. The work is then well swilled in hot water and allowed to dry. It may be finally brushed with a waxed brush. The advantage of this method lies in its rapidity.

COLOURING OF TIN

§ 220. Although tin forms several coloured compounds, such as stannous oxide and sulphide and stannic sulphide, they are scarcely ever employed for bronzing the metal, as the colours obtained are not sufficiently satisfactory. The

best method is to first coat the tin with copper or brass by means of electro-deposition, and then to bronze the electro-deposited surface.

§ 221. We have tested a few solutions for the direct colouring of tin with the results recorded below—

I.	Copper sulphate	120 grains.
	Iron sulphate	120 ,,
	Water	5 fluid ounces.

This solution is best worked hot. The first effect is a deposition of copper, which imparts a brassy appearance to the tin. This colour subsequently becomes deeper and assumes the well-known colour of copper, after which a dark red colour appears on the edges of the work (a stamped tin plate) which gradually extends over the surface as the operation proceeds. On drying out in sawdust and brushing with a waxed brush a good bronze colour remains.

II. A solution of copper sulphate containing 20 per cent of the salt gave a similar result to the former, but a shade darker colour. The result was better with a hot than with a cold solution.

III. A saturated solution of copper acetate acted much slower than the copper sulphate and gave a brassy colour to the tin.

IV. An acid solution of copper sulphate used cold gave a deposit of copper, which being non-adherent washed off when swilled in water, exposing a crystalline tin surface.

V. A solution of copper chloride gave a black deposit on the tin at first, then a red deposit of copper, which afterwards washed off completely by means of water,

leaving a crystallised surface. The same result was obtained in the hot and cold solution.

VI. A solution of equal parts of copper chloride and ammonium chloride gave results identical with those of No. V.

VII. Copper nitrate solution gave a very thin film of copper on the tin, when a cold solution was used; but with a hot solution a white incrustation, probably of metastannic acid, was formed.

VIII. Solutions of ferric chloride, lead acetate, and sodium thiosulphate appear to have no action on tin unless the latter is immersed for a very considerable time, and even then the reaction is but slight. A solution of copper sulphate and sodium thiosulphate gave no result when cold, but a dark deposit was formed when the liquid was heated—this coating, however, easily rubbed off.

CRYSTALLINE SURFACE ON TIN

§ 222. **Moiré Métallique.**—The very beautiful crystalline appearance of tin, to which the above name is given, may very readily be produced by first heating the tin plate to a point where the tin begins to show signs of melting on the edges, and then quenching by immersing the whole in certain cold acid solutions.

The following solution yields excellent results:—

Nitric acid	1 measure.
Sulphuric acid	10 measures.
Water	89 ,,

This gives a surface of small and very numerous crystals.

Much larger crystals and, therefore, fewer in number upon a surface of given area may be produced by pickling the article during a few seconds in a warm acid mixture as above. The metal is immersed when cold. After the immersion it is dried out in sawdust, and varnished with a transparent varnish of any desired colour.

COLOURING OF GOLD

§ 223. **Ormolu Colour.**—To obtain this fine colour on gilt work it is first lightly scratch-brushed, strongly heated, and then allowed to cool a little. The ormolu colouring matter is a mixture of hæmatite, alum, and sea-salt made into a thin paste with vinegar, and applied with a brush until the surface of the article is covered, except such parts as are required to be burnished. The article is heated until it begins to blacken, then removed from the fire, plunged in cold water, washed, and rubbed with a brush which has been dipped in vinegar or dilute nitric acid.

French clocks and other ornamental work are coloured in this way. The gilt articles are lightly scratch-brushed, then coated with a paste of potassium nitrate, alum, and red iron oxide reduced to a fine powder, and worked into a paste with a solution of saffron, annatto, or other colouring matter, according to the tint required. When the gilding is strong, the article is heated until the coating of the above mixture curls over by being touched with the wet finger. When the gilding is only slight,

the mixture is only allowed to remain upon the article for a few minutes. The article is then well washed with water to remove the paste. Such parts as have acquired too deep a colour are afterwards struck with a brush made with long bristles. By a series of vertical strokes with the brush the uniformity of surface is produced. If the first operation has not been successful the colouring is removed by dipping in dilute sulphuric acid, and after well rinsing the operation is repeated.

Red Ormolu is produced by means of a mixture of—

Alum	30 parts.
Potassium nitrate	30 ,,
Zinc sulphate	8 ,,
Common salt	3 ,,
Red ochre	28 ,,
Iron sulphate	1 ,,

To these may be added annatto or madder ground in water.

Yellow Ormolu is produced by the following :—

Potash alum	50 parts.
Red ochre	17 ,,
Zinc sulphate	10 ,,
Common salt	3 ,,
Potassium nitrate	20 ,,

Dead Ormolu, for clocks, is composed of—

Potassium nitrate	37 parts.
Alum	42 ,,
Common salt	12 ,,
Powdered glass and calcium sulphate	4 ,,
Water	5 ,,

The whole of these substances are well ground and mixed with water.

§ 224. **Colouring Gold.**—This operation consists of imparting a colour to gold articles after every other process has been completed. Its object is to give to alloyed gold all the appearance of fine gold itself by dissolving out the base metal from the surface of the articles and leaving a facing of gold of deep rich colour. Two distinct modes of colouring are adopted by jewellers, termed respectively *dry colouring* and *wet colouring*. The latter is most frequently practised, as the former cannot be effectively applied to gold inferior to 18 carat.

Wet Colouring. — The ingredients of the mixture employed in this process have a powerfully solvent action on the base metal with which the gold is alloyed, and a weaker action on the gold itself, so that the article loses weight in direct ratio to the length of time it is submitted to the colouring process, and this loss is greater as the gold is lower in quality. Gee states that the colouring is hastened and the loss in weight reduced to a minimum by using old colouring liquid, and he assumes that the dissolved gold is, to some extent, deposited again on the article, because the loss in weight of some common qualities of gold was found to be very little, and the amount of gold recovered from the spent colouring liquid very small indeed. This statement is in accord with the well-known fact that in any liquid in which a metal, say copper, is electro-positive to the metal in solution, say gold, the latter is deposited on the former.

Many different mixtures are used for colouring gold, some of which will be afterwards given in tabular form.

The following, which he has found to be effective, has been supplied to the author by an experienced Birmingham jeweller :—

Potassium nitrate	12 ounces.
Common salt	6 „
Hydrochloric acid	3 „

The nitrate and salt are pounded to a fine powder and placed in a previously warmed plumbago crucible about 8 inches by 7 inches, then stirred with a wooden spoon for a minute or two. The acid is then added with about 1 ounce of boiling water, and the mass constantly stirred until it boils up to the top of the pot. The work, which has been previously cleansed in hot potash or soda solution, is then suspended in the colouring liquid by means of a silver or platinum wire for about one minute, then well swilled in boiling water. A little more water is added to the colour-pot, and when the liquid boils up the work is again immersed for another minute and swilled in boiling water as before. This operation of dipping and swilling is repeated several times, the colouring liquid being weakened by adding water before each immersion, until the desired appearance is attained. The work is finally well washed in hot water and dried in boxwood sawdust. The whole process takes five to seven minutes.

The coloured work is next scratch-brushed, on a lathe, with a revolving brush made of very fine brass wire and having stale beer dropping on it. If the colouring has been properly conducted, a beautiful rich and dead colour will be produced.

Dry Colouring.—This term is applied to the colouring process when no liquids are used as constituents of the mixture. The ingredients used are—

Potassium nitrate	8 ounces.
Common salt	4 ,,
Alum	4 ,,

These substances are ground to a fine powder, well mixed and placed in a previously heated blacklead "colour"-pot, of the same dimensions as that described for use in wet colouring, but the same pot must not be employed for dry colouring as has been used for the wet process. It is well to get the pot nearly red-hot before placing the "colour" in it. The mixture must then be constantly stirred with an iron rod. It will first boil up as a greenish liquid, then solidify, and afterwards boil up a second time and become thoroughly fused, having a brownish-yellow colour. At this stage the work, which has been previously annealed and dipped in dilute aquafortis, is dipped in the "colour," being suspended on a silver or platinum wire, the latter being preferred, and then kept in motion for about a minute and a half, then immersed in boiling water containing a little aquafortis. The immersion and swilling are again repeated, when the articles possess a beautiful colour. They are then washed in hot water containing a little potash, and finally dried in warm boxwood sawdust.

In dry colouring the work should be as highly polished as possible previous to the colouring, for the brighter it is the better will be the final colour. The time given above is only intended as a general guide, as some work will colour much quicker than others, and the time can only be arrived at by experience. The following mixtures have been recommended for colouring:—

Dry Process.	Wet Process.				
Potassium nitrate 8 oz. Common salt . . 4 ,, Alum . . . . 4 ,,	Potassium nitrate Common salt . . Alum	8 4 4	14 7 7	15 7 7	14 7 ...
Sal-ammoniac . 4 oz. Potassium nitrate 4 ,, Borax . . . . 4 ,,	Hydrochloric acid Water in each case in sufficient quantity. . .	... ...	2 ...	1 ...	5 ...

The following is a useful mixture for removing tarnish from coloured gold which has been kept in stock for some time :—

Sodium bicarbonate	2 ounces.
Calcium chloride	1 ounce.
Common salt	1 ,,
Water	16 ounces.

Well mix the ingredients and apply with a brush.

§ 225. The colour of electro-deposited gold is not the same in every case, but varies in tint according to the nature of the anode and the purity of the solution. If copper goods are gilded in the solution, it becomes charged with some dissolved copper; and the same remarks apply to silver articles, which impart silver to the solution. In the former case the deposited gold becomes redder, and in the latter case paler, yielding what is known as green gold, from the greenish cast of the metal. Red gold may therefore be obtained by adding some copper cyanide to the bath. Green gold is produced by adding some silver cyanide to the gilding bath. By a suitable addition of both silver and copper cyanides a rose-coloured gold is obtained.

Colouring of Gilt Work.—The most simple method is to vary the strength of the current. The old method, which is still practised, is to brush with certain mixtures, such as *gilder's wax*. For a redder colour the wax is prepared with a greater content of copper, while for a greener colour more zinc salt is used. Langbein gives the following :—

I. For red colour. Wax 12 parts, copper acetate 4 parts, zinc sulphate 4 parts, copper scale 4 parts, borax 1 part, red iron oxide 6 parts, copperas 2 parts.

II. For green colour. Wax 12 parts, copper acetate 4 parts, zinc sulphate 8 parts, copper scale 2 parts, borax 1 part, red iron oxide 6 parts, copperas 2 parts.

The wax is melted in an iron pot, and the other ingredients are added, after finely pulverising, in small portions at a time and intimately mixed by stirring till the whole is cold, so that the powder cannot settle on the bottom in lumps. Finally, the soft mass is moulded into sticks one-third of an inch in diameter.

COLOURING OF SILVER

§ 226. The metal silver does not unite directly with the oxygen of the air, so that if no other substance than oxygen were present silver goods would remain unaltered when freely exposed to the atmosphere ; but if sulphuretted hydrogen is present, it attacks the silver in moist air, converting the surface into a layer of silver sulphide, which may vary considerably from a light golden colour to a brownish-black, according to the thickness. If, therefore, a silver article is subjected to the air of a town or other

place where coal-gas is burnt, it gradually changes in colour; and if this change is to be avoided, the article must be coated with a layer of transparent varnish.

The term oxidising then, as applied to the colouring of silver goods, is a misnomer, as oxygen plays but an insignificant part in the colouring; and as the natural tarnishing of silver is chiefly due to sulphur, it would be more correctly termed sulphurising. But the term oxidising has now been accepted in trade and commerce as signifying the colouring of silver by any means; and if we divest it of its strictly chemical meaning, it will suffice to indicate the effect produced, and the term will be used in this sense in the present section.

Various agents are employed in the oxidising of silver, but most of them contain sulphur in some form or other, chiefly as metallic sulphides. In some cases advantage is taken of the fact that some metals when deposited by simple immersion are precipitated on the article in such a fine state of division as to be black, or at least dark coloured. Such is the case with platinum, when deposited from a solution of its chloride, and thus forms one of the most valuable colouring agents for silver.

In addition to the processes which come under the general signification of oxidising, ordinary electro-deposition of other metals on silver is also employed to impart a variety to the pure white surface of the metal. Thus a very minute coating of copper, and then a very thin layer of silver upon that, imparts a dead appearance like frosted silver. Gold of different qualities is also deposited on portions of the surfaces of silver articles to give a variety to their appearance.

In the case of silver alloys, which are chiefly formed of

silver and copper, and consequently have a less white colour than pure silver, their surfaces may be whitened by dissolving out the particles of copper from the alloy, and thus leaving a surface of pure silver. During the manufacture of such alloys into articles, the metal becomes hardened and requires annealing, which consists of making it red-hot and allowing to cool. But as copper is an oxidisable metal and silver is not, the former becomes oxidised by the action of the oxygen of the air, while the silver remains unaltered; and if the whole alloy is pickled in a suitable acid the copper oxide is dissolved out, leaving the surface silver-white in colour. A dilute solution of sulphuric acid is generally employed as a pickle in the above case. A very strong pickle may be formed by dissolving one part of potassium bisulphate in ten parts of water used cold. Should the surface of the article not be clear, it should be well scoured with fine white sand or scratch-brushed.

OXIDISING PROCESSES

§ 227. Some workers recommend the use of a paste similar to that used for bronzing copper, on the assumption that such a mixture is oxidising. But silver is an unoxidisable metal, therefore it would not be affected by the conditions mentioned above. The following mixture was tested :—

Plumbago	60 grains.
Red iron oxide.	10 ,,
Turpentine	to form a paste.

The paste was painted on to the work, allowed to dry,

then rubbed with a clean brush, and lastly with a pad moistened with alcohol. Little, if any, change was produced on the silver, the very slight coloration being simply due to dirt, which was readily removed.

§ 228. Silver goods may be readily coloured by means of a solution of platinum chloride. The platinum chloride may be dissolved in alcohol, ether, or water, according to the effect it is desired to produce. The solution is applied by means of a camel-hair pencil or by means of a linen pad. The process is hastened by making the work warm and vigorously rubbing on the liquid with the pad. The aqueous solution is best applied hot.

The strength of the solution will vary with the depth of colour desired, the more platinum chloride there is present the darker will be the colour and the quicker will be its action. From 1 to 10 per cent of platinum chloride in solution is recommended.

§ 229. The following is a most valuable solution for colouring silver goods :—

Barium sulphide	5 grains.
Water	5 fluid ounces.

This solution imparts a beautiful golden tint to silver, and when worked cold almost any desired shade, from pale to deep gold, may be obtained, according to the time of immersion. If the immersion is continued the gold colour passes through crimson-purple to brown, the former being more or less iridescent. The same colours are obtained by using the solution hot, but they succeed each other more rapidly.

To produce the gold colours it is best to work with a cold solution, because the changes succeed each other more

slowly, and the process can be stopped when the required shade of colour is obtained.

The browns have a rich umber tone, and are very beautiful, passing from very light to very dark shades. It is preferable to work with a warm solution for the lighter shades, and to increase the temperature when the darker tones are required. Scratch-brushing improves the work but renders the colour somewhat paler.

A bluish-black colour may be produced almost immediately by working with a hot solution of twice the strength mentioned above, viz.—

Barium sulphide	10 grains.
Water	5 fluid ounces.

In this latter solution nickel and nickel-plated goods slowly acquire a very beautiful golden-bronze tint, quite different from that produced on silver. In a cold dilute solution a colour something between that of gold and of the English bronze coinage is also produced on nickel.

§ 230. The following is a solution commonly recommended for oxidising silver goods :—

Potassium sulphide . . .	5 grains.
Water	10 fluid ounces.

The variety known as "liver of sulphur" is generally used and imparts a reddish-brown colour to silver, the colour being darker the stronger the solution. This solution should be worked at 60° or 70° C. With a stronger solution than the one given above, the colour produced is bluish-black almost immediately after immersion in the hot solution.

Instead of using potassium sulphide alone some oxid-

isers prefer to add a quantity of ammonium carbonate, thus—

Potassium sulphide	10 grains.
Ammonium carbonate . . .	20 ,,
Water	5 fluid ounces.

This solution worked hot gives a nearly black colour to silver, which assumes a plumbago tint on scratch-brushing.

If the above solution is diluted to double its bulk with water, various shades of brown may be obtained. The colours, however, are not so rich in tone as those produced in a solution of barium sulphide (§ 229).

§ 231. Another solution which produces identical results with the foregoing is composed of—

Potassium sulphide	12 grains.
Ammonium chloride . . .	40 ,,
Water	10 fluid ounces.

It has been recommended to deposit a thin film of mercury on silver goods before oxidising, but there is no advantage gained by this method, except that the action is slower and a bluish-brown colour finally results. With a strong solution the action is quicker and the final colour darker in tone.

§ 232. Ammonium sulphide may be substituted for potassium sulphide in the above recipes. The following results were obtained by its use. The solution was worked at a boiling temperature :—

Ammonium sulphide solution .	20 fluid grains.
Water	10 ,, ounces.

The first result of the immersion of a silver-plated article in the above liquid was to produce various shades of gold,

the colour deepening with the length of time of immersion. These colours were followed by iridescent crimson, umber-brown, and finally a steely-brown.

To obtain a black colour the following proportions should be employed :—

Ammonium sulphide . . .	100 fluid grains.
Water	10 ,, ounces.

Nickel-plated goods simply acquire a dark golden tint in each of the above ammoniacal solutions.

The following modification of the above solution works quicker on a silvered surface but slower on a nickeled surface :—

Ammonium sulphide . . .	20 fluid grains.
Ammonium chloride . . .	40 ,, ,,
Water	10 ,, ounces.

§ 233. The use of sulphuretted hydrogen gas for oxidising silver articles in place of metallic sulphide solutions has been recommended. The articles require to be moistened with water and then fully exposed to the action of the gas. As this gas is very objectionable in consequence of its suffocating odour, the operation should be performed in the open air, or in a fume chamber with a good draught. The method was tried on a silver-plated tray which had been rendered perfectly clean and moistened with water. A stream of the gas was allowed to impinge upon the tray for some time. It would probably be better to enclose the work in a box and to pass the gas first through water and then into the box by means of a suitable orifice. The result obtained in our case was not so satisfactory as with the use of either of

the sulphide solutions before described. The coloration was not uniform.

§ 234. Silver articles may be coloured by means of chlorine, applied either in the form of gas, or as a soluble chloride. When silver is immersed in chlorine water a thin deposit of silver chloride is formed, which darkens on exposure to light.

The following solution has been recommended for producing a warm brown tone on silver :—

Copper sulphate	50 grains.
Ammonium chloride . . .	25 ,,
Vinegar	1 fluid ounce.

A brown colour, with iridescence, was obtained on testing this method, but the film blackened on exposure to light, so that no advantage is gained by its use, and the final result is less effective than with the sulphide solution, especially the barium sulphide method.

§ 235. **Part Gilding and Oxidising.**—Very beautiful effects are produced on metal work by first gilding the articles all over in the usual way, then stopping off certain parts, preferably the most prominent ones, with copal varnish, allowing to dry, then plating the uncovered parts with silver. After rinsing in water the articles may be immersed or painted with one of the before-mentioned oxidising solutions. The varnish is then removed with turpentine.

§ 236. A pink tint may be obtained on silver or silver-plated goods by immersing them for a few minutes in a hot solution of copper chloride, then well rinsing in water, and drying out in sawdust ; or instead of drying, dipping in methylated spirits and igniting the spirit.

PART IV

ELECTRO-CHEMICAL METAL-COLOURING

§ 237. Electricity is often a very important aid in colouring metals, not only because a coloured metal or alloy, such as copper, brass, etc., can be deposited on a white metal like zinc or iron, but because the metal deposited, if sufficiently thick, may be used to take the same chromatic effects as though the whole mass were of the same material as that on the surface. An electric current often hastens a chemical change, so that a metal which only takes a bronze colour very slowly in a certain bath may have the operation considerably accelerated by its use.

A metal or alloy may be deposited on another metal or alloy by simple immersion in a solution of a soluble salt of the metal to be deposited, but the coating thus obtained is always very thin, and thick deposits cannot be obtained in this way. The same remarks apply to the case when the immersed metal is placed in contact with another metal.

Some metals are said to be electro-positive and are represented by the sign +, while others are termed electro-

negative and are represented by the sign −, if then an electro-positive metal is immersed in a solution of an electro-negative metal the latter will be deposited on the former. If, for example, a piece of iron is immersed in a copper solution it will receive a coating of copper. If a piece of a negative metal, such as silver or platinum, is made to touch the immersed iron the deposition will be hastened. In these cases the iron is dissolved and passes into the solution, while the copper passes out of the solution and is deposited on the iron. A good illustration is afforded in the production of the red (Florentine) bronze of Lafleur. A brass article is wrapped round with iron wire and immersed in a very dilute solution of copper sulphate or copper nitrate (spent pickle is generally used), when it soon becomes coated with a layer of copper in a simple and inexpensive way.

The table on p. 273, according to Fischer, represents the metals according to their electrical character :—

In the horizontal lines are the precipitants, and in the vertical lines the metals precipitated. The sign + opposite to zinc, for example, indicates that zinc precipitates gold, osmium, etc., but not nickel as that metal is negative.

It will be seen from this table that some metals are deposited by mere immersion in the solution of another metal, while others are not, because they are of the same electrical order, or more positive than the immersed metal. It seldom happens that a metal is coated by mere immersion in a solution of the same metal. The base metals, zinc, cadmium, tin, lead, and iron become more readily coated than the noble metals, which are very easily deposited by most of the common metals. The solutions of base metals

	Gold.	Osmium.	Iridium.	Platinum.	Palladium.	Rhodium.	Silver.	Tellurium.	Mercury.	Arsenic.	Antimony.	Copper.	Bismuth.	Lead.	Tin.	Nickel.	Iron.
Zinc	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−	−
Cadmium	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−	−
Iron	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−	−
Tin	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−	−
Lead	+	+	+	+	+	+	+	+	+	+	+	+	+	+	−	−	−
Cobalt	+	+	+	+	+	+	+	+	+	+	+	+	+	−	−	−	−
Copper	+	+	+	+	+	+	+	+	+	+	+	+	−	−	−	−	−
Bismuth	+	+	+	+	+	+	+	+	+	+	+	−	−	−	−	−	−
Manganese	+	+	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−
Nickel	+	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
Antimony	+	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
Arsenic	+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−	−
Mercury	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−	−	−
Tellurium	+	+	+	+	+	+	−	−	−	−	−	−	−	−	−	−	−
Silver	+	+	+	+	+	−	−	−	−	−	−	−	−	−	−	−	−
Palladium	+	+	+	+	−	−	−	−	−	−	−	−	−	−	−	−	−
Thallium	+	+	+	−	−	−	−	−	−	−	−	−	−	−	−	−	−

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do not readily yield up their metal. Of all ordinary metals zinc deposits metal from the greatest number of solutions, and appears to have the greatest depositing power.

In reading the foregoing paragraphs it must not be supposed that the deposited metal, whatever its kind may be, always possesses the metallic lustre, as in many cases it has the appearance of a black or dark-coloured film on the surface, and when deposited very rapidly it is thrown down in the form of a dark-coloured or black powder. By rubbing, however, the loose powder may often be removed, and the metal assumes its ordinary colour and lustre.

By the simple immersion process a thin coating only of metal is obtained, and even that is usually imperfect, because the surface to be coated, and the deposited metal, act electrically as two different substances, the former being electro-positive and the other electro-negative. In consequence of this electrical difference there is set up a voltaic action at minute points all over the surface; this action is not perceptible at first because it is of microscopic minuteness, but it gradually spreads from those points all over the surface and causes the metal beneath the coating to dissolve and the deposit to become loose and full of spots.

It is possible, however, to coat a metal perfectly with another metal by means of simple immersion by adopting the following rule, first proposed by Dr. Gore:—Take an electro-positive metal, such as copper, dip it into a solution of a less positive metal, say mercury, when it will receive a coating of mercury. Now immerse it in a third and still less positive metal, say gold; the film of mercury and any parts of the copper which have not been perfectly quicked

dissolve, and a film of gold is deposited in their stead. Now re-dip the copper in the mercury solution, and any still non-coated particles of it are dissolved, and deposit mercury in their place; then dip again into the gold solution and a similar effect takes place as before.

COPPERING BY A SEPARATE CURRENT

§ 238. Zinc, iron, tin, etc., are for the most part coppered by a separate current in alkaline baths, which may be classified into two groups, viz. those containing potassium cyanide, and those without it.

A very good coppering bath may be obtained thus—dissolve $3\frac{1}{2}$ ounces of copper cyanide in a solution consisting of 12 ounces of potassium cyanide and 2 quarts of water, boil, filter off any residue, and then dilute with 6 quarts of water. This bath works very well when heated to 60° or 70° C. Cyanide of copper is not very soluble in cyanide of potassium, the liquid formed does not readily dissolve the anode, nor does it conduct well; it also has a strong tendency to evolve hydrogen at the cathode, but this may be lessened, or wholly prevented, by avoiding the use of any free cyanide of potassium, employing a weaker current, and adding some aqueous ammonia and copper oxide.

§ 239. Watt recommends a solution composed of 1 gallon of water, 6 ounces of potassium cyanide, 4 ounces of potassium carbonate, 2 ounces of liquid ammonia, and 2 ounces of copper sulphate. Dissolve the copper sulphate in distilled water, and when cold add the potassium carbonate and the ammonia. When the

precipitate is redissolved, add the potassium cyanide. Filter off any insoluble matter and employ the liquid for coppering.

§ 240. The following coppering bath is recommended to be used at the ordinary temperature :—Water 10 quarts, crystallised sodium bisulphite 7 ounces, sodium carbonate 14 ounces, neutral copper acetate 7 ounces, pure potassium cyanide 5 ounces, liquid ammonia $4\frac{1}{2}$ ounces. The excess of sodium carbonate serves no useful purpose and had better be omitted, neither is the addition of ammonia necessary.

§ 241. Roseleur recommends the following :—Reduce 20 parts of crystallised copper acetate to powder and rub into a paste with a little water, add to it 200 parts of an aqueous solution containing 20 parts of washing soda, and stir the mixture ; a light green precipitate is formed ; 20 parts of sodium bisulphite are now dissolved in 200 parts of water, and the solution mixed with the former one ; the precipitate becomes a dirty yellow. Lastly, dissolve 20 parts of pure potassium cyanide in 600 parts of water, and add it to the previous mixture. If the solution is not colourless, add more potassium cyanide until it is so. This liquid may be used either hot or cold and requires a current of moderate strength. A current of ·4 Ampère at a tension of 3 to $3\frac{1}{2}$ volts is calculated for 15 square inches of surface of objects.

§ 242. According to Gore another good bath for coppering, which may be employed either hot or cold, consists of 2500 parts of water, 35 parts of pure potassium cyanide, 30 parts of sodium bisulphite, 20 parts of aqueous ammonia, and 35 parts of copper acetate. The cyanide and bisulphite are to be dissolved in one part of the water, and the ammonia

and copper acetate in the other, and the two solutions mixed together. If the blue solution of copper acetate in ammonia does not then become quite colourless, a little more cyanide must be added. If these liquids are used hot the deposition is more rapid. If they become green or blue after working, it is from an excess of copper dissolved, and either the anode should be reduced in size or some potassium cyanide added. If the anode acquires a brown or white insoluble coating, the liquid is deficient in copper, and some more of the copper acetate in ammonia solution must be added. Too large an excess of potassium cyanide causes a strong evolution of hydrogen bubbles on the objects; but no deposition of copper, or only a slight amount takes place, and this has a tendency to peel off. The excess of cyanide can be neutralised by the addition of more copper salt. In any bath containing cyanide, each addition, and especially that of a metallic salt, causes a certain irritation, and causes irregularity of working for some time. Boiling tends to prevent this irregularity.

§ 243. Roseleur specially recommends the following solution for zinc articles:—Water 10 quarts, pure cream of tartar $6\frac{1}{2}$ ounces, crystallised sodium carbonate 15 ounces, copper sulphate $6\frac{1}{2}$ ounces, caustic soda solution of 16° B. $\frac{3}{4}$ lb.

To prepare this bath, dissolve the tartar and sodium carbonate in two-thirds of the water, the copper sulphate in the remaining third, and mix the two solutions. Filter off the precipitate and dissolve it in the caustic soda solution, then add this solution to the former one.

For small zinc objects which require to be coppered in a sieve Roseleur recommends a solution composed of—Water 10 quarts, crystallised sodium bisulphite $1\frac{3}{4}$ ounces,

neutral copper acetate 8 ounces, pure potassium cyanide $8\frac{1}{2}$ ounces, and ammonia $\frac{1}{2}$ ounce.

In preparing copper solutions, the copper acetate prescribed in the preceding formulæ may be replaced by copper carbonate.

§ 244. Dr. Elsner coats base metals with copper by employing a solution composed of—1 part of potassium bitartrate in powder dissolved in 10 parts of boiling water, and as much freshly prepared and wet hydrated copper carbonate added as the liquid will dissolve. The dark blue liquid is filtered and rendered still more alkaline by the addition of a small quantity of potassium carbonate. This liquid may be used to coat articles of tin, cast-iron, and zinc.

§ 245. Gauduin's coppering solution consists of a solution of copper oxalate with ammonium oxalate and free oxalic acid. It is said to work well when heated to about 70° C.

§ 246. In preparing cast-iron work for electro-coppering, after the pieces have been pickled and scoured, they should be carefully examined for sand-holes, and if any such cavities appear on the work, they must be well cleared from dirt by means of a steel point. After this, well brush again with sand and water. It is a good plan to give the article a slight coating in the coppering bath, and then examine to see if any places are uncovered. The body should have a final brushing with moist sand, then well rinsed in clear water, and put into the coppering bath. The alkaline bath should only be used to give a complete covering of copper and the article should then be transferred to a copper sulphate bath to finish.

If the current is too great in relation to the surface of

the work, the copper is deposited as a brown or brownish-black powder. In the sulphate solution, if the liquid is too dense, streaks are apt to be formed on the receiving surface, and the article (especially if a tall one) will receive a thick deposit at its lower part, and a thin one at the upper portion, or even have the deposit on the upper end redissolved. If there is too little water, crystals of copper salt form on the anode and at the bottom of the vessel. The copper obtained from the usual double cyanide of copper and potassium solution by a weak current is of a dull aspect, but with a strong current it is bright.

BRASSING BY A SEPARATE CURRENT

§ 247. A brassing solution may be made of different proportions of copper cyanide and zinc cyanide, or other copper and zinc salts dissolved in a suitable solvent; and since a solution of copper cyanide requires a different current strength from one of zinc salt, it will be seen that, according to the greater or smaller current strength, now more of one, now more of the other metal is deposited, which influences the colour of the deposit. Hence the proper regulation of the current is the chief condition for obtaining good deposits. For solutions containing two or more metals the less positive one is generally deposited first if the current is weak. In a brassing solution, with a weak current, the copper is largely deposited, while a more powerful current deposits both copper and zinc; if too strong, zinc will be chiefly deposited. A solution containing copper and zinc salts in about equal proportions is considered to be the most suitable and the least subject to fluctuations.

In making a solution for the deposition of the alloys, brass, bronze, German silver, etc., Watt recommends that, instead of forming a solution from the salts and their solvents, the alloy should be dissolved in nitric acid, and from the acid solution thus obtained the depositing bath should be formed. Metals of the best quality should be used and the anode should be formed of the same quality of alloy as that used in making the solution.

§ 248. One gallon of a good brassing solution can be made according to the method referred to in the last paragraph by taking

Good brass	1 ounce.
Nitric acid	4 ounces.
Water	4 „

Cut up the brass into small pieces, place in a glass beaker, add the water and then the acid. The beaker should be gently heated on a sand-bath in a fume chamber so that the fumes may pass into the flue of the chimney. When the acid is completely exhausted, the red fumes will cease to come off. If the whole of the brass has been dissolved before the acid is exhausted some more of the metal must be added, and the heat continued until the acid fumes cease, while some undissolved metal remains in the flask, so as to prevent excess of acid.

The acid solution must be poured into a larger vessel, diluted with three or four times its bulk of water, and liquid ammonia added, until the precipitate which first forms is redissolved (stirring the liquid in the meantime with a glass rod) and a clear blue solution is obtained. A moderately strong solution of potassium cyanide must

now be added to the solution with constant stirring until the blue colour entirely disappears, leaving a yellow-tinted solution. A moderate excess of free cyanide is then added, and the solution made up to a gallon with water. The solution must be allowed to rest for a few hours and the clear liquid poured from the sediment into the plating vessel. If the solution is to be used hot it may be further diluted with water.

§ 249. Roseleur recommends the following :—

Copper sulphate	$5\frac{1}{4}$ ounces.
Zinc ,,	$5\frac{1}{4}$,,
Sodium carbonate (crystallised)	$15\frac{3}{4}$,,
,, bisulphite	7 ,,
,, carbonate (crystallised)	7 ,,
Potassium cyanide (pure)	$8\frac{3}{4}$,,
Arsenious acid	$30\frac{3}{4}$ grains.
Water	10 quarts.

The bath is prepared by dissolving the copper and zinc sulphates in one portion of hot water, and the $15\frac{3}{4}$ ounces of sodium carbonate in another portion; mix the two solutions and well stir. The copper and zinc are precipitated as carbonates, and the vessel with its contents is allowed to rest until the precipitate subsides, when the clear liquid is poured off and thrown away. Now add, without washing the precipitate, about 6 quarts of water, and dissolve in it, with constant stirring, the 7 ounces each of sodium carbonate and bisulphite, adding these salts a little at a time. Dissolve the potassium cyanide in 4 quarts of cold water, and add this solution, with the exception of about half a pint, in which the arsenious acid is dissolved, to the first solution, and finally add the solution

containing the arsenious acid. If the solution is not clear after well stirring, more potassium cyanide must be added.

Brassing solutions, as a rule, work more irregularly than other cyanide baths, the deposit being too red or too gray, while occasionally one side of an object is coated well and the other not at all. To force the solution to work well it should be thoroughly boiled, and the water lost by evaporation replaced. If boiling is not admissible, then the solution must be worked through for some hours with the current, until it gives the right colour. The addition of the arsenious acid is said to make the brassing brighter, but if the above-mentioned proportion is exceeded, the deposit will be too light and show a gray tone.

§ 250. Another brassing solution is composed of

Sodium carbonate . . .	10½ ounces.
Crystallised sodium bisulphite .	7 ,,
Copper cyanide	3½ ,,
Zinc ,, ...	3½ ,,
Water	10 quarts.
Potassium cyanide . . .	till solution is clear.

The sodium carbonate and bisulphite are dissolved in two to three quarts of water. The cyanides of copper and zinc are rubbed to a thin paste with water in a porcelain mortar; the paste is then added to the solution of sodium salts, and the potassium cyanide added with brisk stirring, until the metallic cyanides are dissolved. Dilute to ten quarts.

§ 251. A simple brassing solution may be rapidly made by using

Copper sulphate .	1 part.
Zinc ,, . .	1 ,,
Water . . .	sufficient to dissolve the salts.
Potassium cyanide .	...
Ammonia . . .	...

The copper and zinc sulphates are dissolved in water and potassium cyanide added, with brisk stirring, until the precipitate first formed redissolves; to the resulting solution one-tenth to one-fifth liquid ammonia is added and the solution diluted moderately with water. For a light-coloured brass two parts zinc sulphate to one part of copper sulphate are used.

§ 252. For coating iron, steel, and tin with brass the following solution of Roseleur's may be used :—

Sodium bisulphite	2 parts.
Potassium cyanide (75 per cent)	5 ,,
Sodium carbonate	10 ,,
Distilled water	80 ,,

Then add to the above solution

Fused zinc chloride	1 part.
Copper acetate	1¼ parts.
Water	20 ,,

§ 253. All work which has to be electro-brassed must be scrupulously clean. Cast-iron work may be pickled in a solution of

Sulphuric acid	½ pound.
Water	1 gallon.

Scoured with sand and swilled with water. If the iron articles are coated with rust, it may be removed by brushing with sand and strong hydrochloric acid, after which they should be immersed in the sulphuric acid pickle.

Zinc articles are prepared for brassing by pickling in

Sulphuric acid	1 ounce.
Hydrochloric acid	2 ounces.
Water	1 gallon.

After pickling the work is well rinsed, scoured with sand and water, then swilled and placed in the brassing bath. Iron and zinc articles should not be suspended in the bath at the same time if it can be avoided, and if this is not convenient, the iron articles should enter the bath first, and when they have been coated all over, the zinc work may be introduced.

In brassing, the distance of the objects to be coated from the anodes is of considerable importance. If objects with deep depressions or high reliefs are hung in a brassing bath, it is sometimes found that the relief parts are paler in colour than the groundwork, which will show a redder deposit; in such a case the distance from the anode must be increased. After an electro-brassing bath has been in use for some time, its whole character may be altered, because (1) the anode is composed of two metals of unequal solubility in potassium cyanide, and does not therefore maintain the solution constant; (2) as ammonia is often a constituent of the plating bath, this, being a volatile body, evaporates during the working and therefore alters the composition of the solution; (3) the zinc oxide liberated at the brass anode becomes less soluble than the copper oxide set free at the same electrode, and the free cyanide in the solution is largely taken up by the latter to the exclusion of the less soluble zinc oxide; in this way the solution becomes more highly charged with copper than with zinc; (4) when a current of low electro-motive force is used in depositing brass, the copper is more readily deposited than the zinc, and *vice versa*; (5) the amount of anode surface immersed in the solution in proportion to that of the cathode sensibly affects the deposition of brass; if, for example, the anode surface is very large compared

with the surface to receive the deposit, zinc will be principally deposited, but if the opposite condition prevail, then copper is deposited.[1]

DEPOSITION OF BRONZE BY A SEPARATE CURRENT AND BY CONTACT

§ 254. The electro-deposition of an alloy of copper and tin, known under the general name of bronze, may be performed in a similar manner to that of brass, by substituting a salt of tin in place of a salt of zinc.

For coating wrought and cast iron with bronze, Gountier recommends the following solution :—

Potassium ferrocyanide . . .	10¼ ounces.
Cuprous chloride	5¼ ,,
Tin chloride	14 ,,
Sodium thiosulphate	14 ,,
Water.	10 quarts.

Elsner prepared a bronzing bath by dissolving 21 ounces of copper sulphate in 10 quarts of water, and adding a solution of 2½ ounces of tin chloride in caustic potash.

The above methods are far from satisfactory, and as the various bronze shades may be closely imitated by depositing different qualities of brass, by altering the proportions of copper and zinc, varying the current, etc., the deposition of bronze is rarely required.

§ 255. Langbein states that the following bath is reliable :—Prepare, each by itself, solutions of copper phosphate and stannous chloride in sodium pyrophosphate. From a copper sulphate solution, precipitate copper phosphate by means of sodium phosphate, allow the precipitate to settle, and after pouring off the clear supernatant liquid, bring it

[1] Watt's *Electro-Deposition*, p. 382.

into solution by means of a concentrated solution of sodium pyrophosphate. On the other hand, add to a saturated solution of sodium pyrophosphate the solution of the tin salt as long as the milky precipitate at first formed redissolves. To these two metallic solutions add a solution of sodium pyrophosphate, which contains about $1\frac{3}{4}$ ounces of the salt to the quart, until the precipitate appears quickly and of the desired colour. Some sodium phosphate requires to be added to the bath from time to time, and if the colour becomes too light, solution of copper, and if too dark, solution of tin.

§ 256. Mr. Fred Wiels deposits bronze on iron, steel, and other metals by means of a solution of

Sodium-potassium tartrate	150 parts.
Water	1000 ,,
Soda lime (containing 50 to 60 per cent of free soda and 35 per cent of copper sulphate) . .	80 ,,
Tin chloride in sodium hydrate	80 ,,

The iron or steel articles are cleaned in dilute sulphuric acid, washed with water, and finally with water made alkaline with soda, then scratch-brushed, again swilled and immersed in the plating bath in contact with a piece of lead or zinc, or suspended by zinc wires.

M. Weiss Kopp imparts a bronze colour to electro-coppered articles of cast-iron, by rubbing them with a mixture of 4 parts of sal-ammoniac, 1 of oxalic acid, and 1 of acetic acid, dissolved in 30 of water.

DEPOSITION OF NICKEL AND ITS ALLOYS

§ 257. A solution of nickel for plating by means of a separate current may be made by dissolving the double sulphate of nickel and ammonia in water, in the proportion

of 12 ounces of salt to the gallon. The solution should be tested with blue litmus paper, and if the paper is turned red, it shows an excess of free acid which must be neutralised by cautiously adding ammonia until the liquid is slightly alkaline. Or a nickel-plating solution may be made by suspending a large plate of nickel in dilute sulphuric acid, and placing it in contact with the positive pole of the battery. The negative pole is joined to a small plate of nickel which is also suspended in the solution. A current is then passed until sufficient nickel has been dissolved from the anode, which is determined by weighing it before and after passing the current; the solution is then neutralised with ammonia. To each ounce of nickel sulphate in solution add one ounce of ammonium sulphate, and test with litmus paper as described above. All articles to be nickel-plated are required to be scrupulously clean and previously polished bright.

As nickel solutions are used in the concentrated state the nickel salt begins to crystallise after a time, especially in a warm place, in which case water must be added. It should also be borne in mind that the anode does not maintain the strength of the solution, so that it is necessary to add crystals of the double salt from time to time to replenish the weakened solution.

In nickeling iron, zinc, etc., the articles should be first covered with a strong current, and then a weaker current may be employed to finish with.

§ 258. An alloy of nickel and cobalt possesses greater hardness than either of the metals separately, and Langbien states that the greatest degree of hardness is attained with nickel 70 to 75 parts, and cobalt 30 to 25 parts. The most suitable plating baths are as follows :—

Nickel-ammonium sulphate . .	21 ounces.
Cobalt-ammonium sulphate . .	$5\frac{1}{4}$,,
Ammonium sulphate . . .	9 ,,
Water	15 quarts.

Instead of ammonium sulphate, $10\frac{1}{2}$ ounces of boric acid may be used.

For the first bath the salts are dissolved in water, and in case the liquid is too acid, ammonia is added until blue litmus paper is only slightly reddened. It is best to use rolled and cast anodes in equal proportions; and when the bath becomes alkaline to restore its original slightly acid reaction by the addition of a little citric acid.

The second bath must not be neutralised but worked in its strongly acid reaction. If after dissolving the double nickel and cobalt salts the solution is acid, the free sulphuric acid should be neutralised by one or two ounces of nickel carbonate, then the solution acidified by the boric acid.

§ 259. Stolba recommends the following solution for nickeling by zinc contact without the aid of a battery :—

Heat a boiling concentrated solution of zinc chloride in a copper kettle, with double its volume of soft water, then add, drop by drop, pure hydrochloric acid until the precipitate formed by diluting the zinc chloride solution with water disappears. Then add as much zinc powder as will lie on the point of a knife, the effect being that the copper of the kettle, as far as it comes in contact with the solution, is in a few minutes zinced. Now bring into the kettle sufficient nickel sulphate to colour the liquid perceptibly green, then introduce the articles to be nickeled, together with small pieces of zinc or zinc wire so as to present many points of contact, and continue boiling.

With a proper attention to the details it is claimed that the articles will be uniformly nickeled in fifteen minutes; if such is not the case the boiling must be continued, fresh pieces of zinc added, or, if the solution does not look sufficiently green, fresh nickel salt introduced.

For the success of the process the articles must be perfectly clean. The solution must not become turbid on boiling by the separation of basic zinc salt, nor acid by free hydrochloric acid, otherwise the nickeling will be dull and blackish. The turbidity is removed by cautiously adding drop by drop some hydrochloric acid, and any acidity by means of sodium carbonate. The articles after plating are well swilled, dried, and polished with whiting.

The above method of nickeling may also be carried out for iron and steel articles with the zinc contact. To a 10 per cent zinc chloride solution add enough nickel sulphate to impart a deep green colour, and heat to the boiling point. Then, without troubling about the turbidity caused by the separation of basic zinc salt, immerse the articles in it so as not to touch each other, and keep the whole boiling for thirty to sixty minutes, replacing the water lost by evaporation in the meantime. The deposition of metal is of course very thin.

§ 260. By boiling a mixture of $8\frac{1}{2}$ ounces of nickel-ammonium sulphate and $8\frac{1}{2}$ ounces of ammonium chloride in 1 quart of water, together with clean iron filings, and introducing into the liquid the copper or brass articles, the latter become coated with a thin layer of nickel. The nickel solution requires to be frequently renewed.

§ 261. German silver, an alloy of copper, zinc, and nickel, may be deposited on other metals, according to Watt, by dissolving a portion of the alloy (say one ounce) in

nitric acid, taking care to leave a little undissolved metal at the finish so as to ensure that the free acid has been completely taken up, then pouring off the clear solution. Now dissolve 4 ounces of potassium carbonate in a pint of water, and add this solution gradually to the former solution with careful stirring until no further precipitation takes place. The precipitate must be washed several times with hot water and then redissolved by adding a strong solution of ammonia in about the right quantity to just redissolve it, and sufficient potassium cyanide to decolorise it. A little excess of potassium cyanide is then added to form free cyanide, and the bath worked with a German silver anode. The battery power required would be the same as that used for working a brassing solution.

DEPOSITION OF SILVER BY A SEPARATE CURRENT

§ 262. The preparation of a silver-plating solution comprises three distinct operations, viz.—

(*a*) The conversion of silver into silver nitrate.

(*b*) The precipitation of the whole of the silver from the above solution, as silver cyanide or chloride.

(*c*) The conversion of the insoluble cyanide or chloride into the soluble double cyanide of silver and potassium.

Note.—Distilled water or filtered rain water should always be used.

It is assumed that the potassium cyanide used in making the following solution contains 75 per cent of KCy :—

To prepare one quart of solution, proceed as follows :—Put 240 grains of fine silver in an evaporating dish,

cover with nitric acid diluted with an equal bulk of water, and heat gently on a sand bath until dissolved. If the action becomes violent, add a little cold water, and remove the source of the heat. Any excess of acid should be avoided. Evaporate cautiously to dryness to expel the free acid, and dissolve the residue (which is silver nitrate) in water, and make up the solution to a quart with distilled water.

Make a solution of potassium cyanide by dissolving 200 grains in about 4 ounces of water, and add it in successive small portions to the silver nitrate solution, with brisk stirring, until a precipitate ceases to form in the clear liquid. If too much cyanide is added, some of the precipitated silver cyanide will be dissolved. Allow to stand till clear, then decant the clear liquid, and well wash the precipitate several times with water.

Dissolve 400 grains of potassium cyanide in 4 ounces of water, and transfer the solution to a tall glass jar. Make a paper scale, divided into inches and eighths, paste it upon the jar, and note the level of the solution. Add this solution to the precipitated silver cyanide, with brisk stirring, until a very small portion remains undissolved. The solution is the double cyanide of silver and potassium. Observe by reference to the paper scale the proportion of potassium cyanide solution used, then add an equal quantity to supply the necessary amount of "free cyanide"; add sufficient water to make the solution up to one quart, and filter. It is then ready for use. This forms one of the best silver-plating solutions.

§ 263. When deposited silver is required to have a dead pearly-white appearance, a solution prepared as follows should be used—

Prepare a solution of silver nitrate as before, and precipitate the silver with hydrochloric acid in excess. Well wash with hot water until the wash water ceases to redden blue litmus paper. Dissolve 600 grains of potassium cyanide in 6 ounces of water, and transfer to the glass jar containing the paper scale mentioned in the previous experiment. Add the solution gradually to the silver chloride precipitate, stirring the whole time until it is almost completely dissolved.

Read off the proportion of cyanide used, and add one-half more for "free cyanide." Make up to one quart with water, and filter for use.

When the percentage of potassium cyanide in the commercial article is known, much time may be saved by adding the exact quantity required to precipitate the silver as cyanide. This quantity is found by multiplying the weight of silver by 0·6 and by the reciprocal of the percentage.

§ 264. **Battery Method of making a Silver-Plating Solution.**—Dissolve 2 ounces of potassium cyanide in 1 quart of water; place in this liquid a silver plate to form the anode, and a much smaller silver plate for the cathode. Pass a current through the solution until a piece of bright German silver the same size as the anode receives a good deposit when it is made the cathode in place of the small silver plate. Or pass the current until $\frac{1}{2}$ ounce of silver is dissolved from the anode.

Copper, brass, and German silver work should be "quicked" immediately before plating. The quicking solution may be prepared as follows—

Dissolve $\frac{1}{4}$ ounce of mercuric oxide in a strong sclution of potassium cyanide. Note how much of the potassium

cyanide solution was used to dissolve the red powder, and then add one-half of that quantity for free potassium cyanide, and make up the bulk of the solution with water to one quart.

The work should be dipped in this solution until it becomes uniformly white. It should then be rinsed in water and immersed in the plating solution to receive a deposit of silver.

Work that has been quicked before plating is less liable to strip in undergoing the subsequent processes of scratch-brushing and burnishing.

Iron, steel, and zinc should be coppered in the cyanide bath before silvering.

Pewter, Britannia metal, etc., are usually steeped in a hot potash solution and transferred without riusing to a "plating solution," containing a large excess of potassium cyanide, in which it is "struck," with a current dense enough to give evidence of incipient burning of the deposit. When struck the work is scratch-brushed, and transferred to an ordinary plating solution to receive its final deposit. A beginner would no doubt find it easier to treat these metals as he would iron and zinc by first giving them a coat of copper in the cyanide bath.

DEPOSITION OF GOLD ON OTHER METALS

§ 265. Gold is dissolved in aqua regia in the same way that silver is dissolved in nitric acid. The solution of gold chloride is evaporated over a water bath nearly to dryness to expel excess of acid, and the residue is dissolved in a small quantity of water. To the concentrated solution add a solution of good potassium cyanide

as long as a precipitate of gold cyanide is formed. Well wash the precipitate, and then add just sufficient potassium cyanide solution to dissolve it. Afterwards add, say one-fourth of the quantity of potassium cyanide used in dissolving the precipitate, to give the requisite amount of "free cyanide."

Another method of preparing a gilding solution is to precipitate the gold as fulminate by adding ammonium hydrate to a dilute solution of chloride of gold until the precipitate ceases to form. Thoroughly wash the precipitate, and whilst it is still wet add a solution of potassium cyanide until it is exactly redissolved. Add free potassium cyanide as in the former method.

Notes.—Fulminating gold is very explosive when dry. The precipitate must therefore be dissolved in potassium cyanide immediately after washing.

This solution is more easily prepared than the preceding one, and works well.

Gold-plating solutions may be also prepared by the battery method in a similar manner to that described for silver, but it is necessary to use 2 ounces of potassium cyanide per pint of water, and to substitute a gold anode and cathode for the silver ones. This is the best method for non-chemical students.

All these solutions should be worked at about 150° F., with a gold anode, and with a current from two Bunsen cells arranged in series.

A good gilding solution should contain one ounce of gold per gallon, but a solution containing less than half that amount will work fairly well.

§ 266. **Recovery of Gold from Old Solutions.**—1st Method. Add hydrochloric acid in excess to the solution,

in the open air or in a fume chamber, so as to avoid inhaling the fumes of hydrocyanic acid, syphon off the clear liquid and collect the cyanide of gold. Dissolve it in aqua regia, evaporate nearly to dryness, add water, and precipitate the gold with ferrous sulphate.

2nd Method. Evaporate the solution to dryness, ignite the residue, dissolve the saline mass in water, and finely-divided gold remains. Dissolve this gold in aqua regia, and recover it, as in the first method, by precipitating it with ferrous sulphate.

§ 267. **Recovery of Silver from Old Solutions.**—Add hydrochloric acid in excess, syphon off the clear liquid, collect the precipitated silver chloride, dry and fuse in a clay crucible with twice its amount of sodium carbonate and a little nitre, pour into mould, allow to cool, and detach the slag by striking it with a hammer. Or the solution may be evaporated to dryness, the residue fused at a red heat, the soluble matter dissolved in water, and the finely-divided silver fused with carbonate of soda as before.

§ 268. **Water Gilding.**—This is the name given to the method of gilding by simple immersion. The following was patented by G. R. Elkington of Birmingham and carried on for some time in that city :—

Hydrogen potassium carbonate . .	60 parts.
Gold chloride	1½ ,,
Water	200 ,,

The mixture is boiled for two hours, during which period the solution, at first yellow, assumes a green colour, when it is completed. Brass and copper articles are gilt by dipping them for about half a minute in the hot solu-

tion. German silver goods require to be placed in contact with a zinc or copper wire.

§ 269. According to Langbein the two following methods have stood the test of experience :—

I.	Crystallised sodium pyrophosphate . .	$2\frac{3}{4}$ ounces.
	12 per cent prussie acid	$4\frac{1}{2}$ drachms.
	Crystallised gold chloride	$1\frac{1}{8}$,,
	Water	1 quart.

Heat the mixture to the boiling point, and immerse the objects of copper and its alloys in the liquid with constant moving until they are gilded. Iron, steel, tin, and zinc articles should be previously coppered. Baths containing sodium pyrophosphate give good results when fresh, but they quickly decompose and can seldom be completely exhausted. In this respect No. II. is better.

II.	Crystallised sodium phosphate . . .	$2\frac{3}{4}$ drachms.
	Pure caustic potash	$1\frac{1}{2}$,,
	Gold chloride	$\frac{1}{2}$,,
	Potassium cyanide	9 ,,
	Water	1 quart.

Dissolve the sodium phosphate and the potash in part of the water, and the gold chloride and the potassium cyanide in the other part. Mix the two solutions together, and boil for use as before. It is best to dip the articles in the partly used solution and finish in a freshly prepared one. The deposit of gold by simple immersion is, in all cases, very thin.

ELECTRO-CHROME

§ 270. Nobili, in the year 1826, discovered that when a solution of lead acetate is electrolysed, by means of a strong current, using a large platinum anode and a

platinum wire cathode, a deposit is formed on the anode; and that if a polished steel plate be employed as the anode, using a current from 6 Groves cells, the deposit is in the form of a thin film, and exhibits all the colours of the spectrum. By placing the anode horizontally beneath the vertical cathode wire the colours are in the form of rings concentrically arranged round the wire which forms the centre and in the order of the chromatic scale. These are known as Nobili's rings. The experiments may be conducted in the following way:—

Make a concentrated solution of lead acetate by boiling lead acetate with water, filter off any insoluble residue, and pour the clear liquid into a shallow dish. A plate of polished steel is then immersed in the solution and allowed to rest on the bottom of the dish; it is connected with the positive pole of the battery or dynamo. A small disk of copper is joined with the negative pole of the battery by means of a wire. If now the copper plate be brought as near as possible to the steel plate without touching it, in a few moments a series of beautiful prismatic colours will appear upon the steel surface, when the plate should be removed and well swilled in water.

The effect is due to the deposition of thin films of lead peroxide, the varied hues being occasioned by the different thicknesses of this film, the light being reflected through them from the polished metallic surface beneath. By reflected light every prismatic colour is visible, and by transmitted light a series of prismatic colours complementary to the first series will appear, occupying the place of the former series. The colours are seen to the greatest advantage by placing the plate before a window with its back to the light, and holding a piece of white

paper at such an angle as to reflect the light upon its surface. The colours appear very durable and will bear a considerable amount of friction without being removed. If the deposition continue too long the coloration will be less marked and become more or less red, green, or brown. If well rubbed, when dry, with the finger a rich blue-coloured film will be laid bare, by the removal of the delicate film above it.

Becquerel, Gassiot, and others have, by varying the strength of the battery and of the solutions employed, and interposing non-conducting patterns between the anode and cathode, and by using cathodes of different shapes, obtained effects of great delicacy and beauty.

The following formula is due to Becquerel:—Dissolve $\frac{1}{2}$ lb. of caustic potash in 2 quarts of distilled water, add $5\frac{1}{2}$ ounces of litharge, boil the mixture for half an hour and allow the residue to settle. Pour off the clear liquid, dilute with an equal bulk of water, and use the solution when cold for the deposition. The solution is rapidly deprived of its metal, because lead is deposited on the cathode at the same time.

Mr. Gassiot's method to obtain "metallo-chromes" is to place over the steel plate a piece of card, cut into some regular device, and over this a rim of wood, the copper disk being placed above this as before. One of the simplest plans is to turn up a piece of copper wire in the form of a ring, cross, or star, and connect it with the positive pole of the battery.

Metallo-chromy is used to ornament metallic toys, for colouring bells, and the hands and dials of watches, by means of Becquerel's solution.

Salts of other metals, such as manganese, bismuth,

cobalt, nickel, etc., which yield deposits of peroxide at the anode, may be employed instead of those of lead. Watt has produced excellent effects on nickel-plated goods in this way. By this means may be imparted to different polished surfaces all the richest colours of the rainbow. They commence with silver blonde, and progress onwards to fawn colour, and thence through various shades of violet to the indigo and blues; then through pale blue to yellow and orange; thence through lake and bluish-lake to green and greenish-orange and rose-orange; thence through greenish-violet and green to reddish-yellow and rose-lake, which is the highest colour on the chromatic scale.

The colours occur sometimes on the anodes, and sometimes on the cathodes, according to the liquid employed, and with a variety of metals in a number of different liquids. At other times they arise wholly from deposits from the liquid, as with peroxides on anodes of platinum, or films of metal upon the cathodes; and sometimes they consist of insoluble substances formed by the union of the anode with an element of the liquid.

COPPERING ZINC, IRON, STEEL, TIN, LEAD, BRASS, ETC., BY SIMPLE IMMERSION AND BY CONTACT WITH ANOTHER METAL

§ 271. A simple solution for coppering zinc by simple immersion may be employed as follows—

Copper sulphate . .	250 grains.
Water	8 fluid ounces.
Ammonia . . .	to precipitate and redissolve.

The copper sulphate is dissolved in the water, and liquid ammonia added until the green precipitate which

forms at first is redissolved and a deep blue coloration results. The solution imparts a bright deposit of copper on zinc when there is a slight excess of ammonia present. If the solution is just neutral or only slightly alkaline the deposit of copper is more or less dull.

The deposit obtained in the hot solution appears to be thinner and paler than that obtained in the same solution when cold. Doubtless this is due to the greater solubility of copper in hot ammonia solution. If the deposit is gently scratch-brushed, the reduction of thickness produced by this means causes the coating to appear brassy, and if the scratch-brushing is vigorously applied the whole of the deposit is removed. The deposit is therefore very thin but reguline, and firmly adherent to the zinc.

Evidence of deposition of copper upon iron was obtained, but the coating was not reguline in character, and only obtained with difficulty. By immersing iron in contact with zinc no better result was obtained. Lead and tin were uncoppered even after a considerable time of immersion with or without contact with zinc. No reaction was obtained on brass by immersion in this solution without it was in contact with zinc or iron.

A modification of this method is recommended by Gräger for coppering large articles of zinc, steel, and iron. He employs two solutions, (*a*) and (*b*). The following proportions were used in our experiments :—

(*a*)	Hydrochloric acid .	1 fluid ounce.
	Water . . .	1 ,,
	Zinc chloride . .	½ ounce.
(*b*)	Copper sulphate .	½ ounce.
	Water . . .	8 fluid ounces.
	Ammonia . .	to precipitate and redissolve.

The clean article is first painted all over with the solution (*a*), and while it is still moist a coating of the solution (*b*) is imparted.

Zinc is coppered by solution (*b*) alone without the assistance of solution (*a*). Iron is well coppered by using both solutions as directed above. Tin is not coppered unless it is in contact with zinc, when it becomes coated with copper at the point of contact only. The coating is very thin and is easily removed with the scratch-brush. Brass was not coppered even in contact with zinc. The solution (*b*) becomes turbid on working and requires the addition of ammonia occasionally.

§ 272. Elsner recommends the following solution for coppering cast-iron goods. The proportions given below are those used in our experiments :—

Copper sulphate	1 ounce.
Water	5 fluid ounces.
Potassium hydrate	in excess.

The amount of potassium hydrate employed was determined by the quantity required to just precipitate the whole of the copper as black copper hydrate. The precipitate was then well washed and dissolved in a concentrated solution of sodium bisulphite. 1200 grains of the bisulphite were used, but a slight brown residue was left undissolved.

It is an excellent solution for coppering sheet iron and wire as well as for cast iron. Zinc receives a black deposit, so that a solution of the above strength is not suitable for coppering that metal, although the deposit may be greatly improved by subsequent rubbing with whiting. Tin and brass do not become coated by simple immersion in this solution, but the latter when in contact with zinc receives

a good reguline deposit, which is rendered paler in colour by scratch-brushing.

§ 273. According to Bacco a solution of the double cyanide of copper and potassium is used for coppering zinc by simple immersion, and for coppering iron by immersion in contact with zinc. The following results were obtained by us :—

(*a*)	Copper sulphate . . .	1 ounce.
	Water	5 fluid ounces.
(*b*)	Potassium cyanide . .	1¼ ounces.
	Water	5 fluid ounces.

The solution (*a*) was added to (*b*) and the precipitate of copper cyanide which was formed at first was redissolved, yielding a clear coffee-coloured solution containing some free potassium cyanide.

No deposit of copper was obtained upon either zinc, iron, or tin by simple immersion. The solution was then divided into two equal portions, A and B.

Copper sulphate was added to A until a precipitate was just produced. In this solution zinc was imperfectly coppered. To the solution B 250 grains of pure potassium cyanide were added. No effect was produced by the immersion of zinc, iron, or tin.

In adding potassium cyanide to copper sulphate a copious evolution of hydrocyanic acid takes place, and care must be taken not to inhale this gas, as it is a powerful poison.

§ 274. A solution of copper tartrate in potassium tartrate has been recommended for coppering zinc. The following proportions were tried :—

Cream of tartar . . .	100 grains.
Copper tartrate . . .	10 ,,
Water	8 fluid ounces.

The solution was rather turbid from excess of copper tartrate. The cold solution gave a fairly bright deposit on iron immediately after immersion, but on swilling the same and drying out in sawdust the deposit assumed a brassy colour, which, on scratch-brushing, completely disappeared, exposing the bright iron surface. No deposit of copper was obtained in the cold solution upon either zinc, tin, or brass. When the solution was made hot it failed to copper either iron, zinc, tin, or brass.

Ammonia was added to the above solution in slight excess, and the same was tried both hot and cold without yielding a deposit of copper to either of the above-named metals.

§ 275. The following modification of the above method is due to Ludersdorff.

Copper sulphate . . .	250 grains.
Water	3 fluid ounces.

The solution was then treated with a solution of

Sodium carbonate (crystallised) .	500 grains.
Water	5 fluid ounces.

The precipitate of copper carbonate was allowed to settle, filtered, and washed. Then a solution was made of

Cream of tartar	400 grains.
Water	8 fluid ounces.

The solution thus formed was used to dissolve the precipitate of copper carbonate, and when the solution was clear it gave an acid reaction.

Iron and tin were coppered in this liquid when cold by placing in contact with zinc. Both iron and zinc received a good bright deposit of copper in the hot solution. In the cold solution the deposit was darker and less brilliant than that obtained by means of the hot solution.

§ 276. Hess recommends the following method of preparing a copper tartrate solution :—First dissolve copper sulphate in water and add to it a solution of sodium hydrate and cream of tartar. The following proportions were tried :—

(*a*)	Copper sulphate	240 grains.
	Water	4 fluid ounces.
(*b*)	Cream of tartar	440 grains.
	Sodium hydrate	440 ,,
	Water	4 fluid ounces.

The solution (*a*) was added to solution (*b*), when a blue and alkaline liquid resulted.

The cold solution gave a bright deposit of copper upon zinc, but no effect was obtained upon brass, iron, or tin. A good deposit of copper was formed on iron and brass by the aid of a zinc contact but not upon tin. The same solution when hot does not appear to be suitable as it deposits copper in a more or less dark or powdery condition.

Instead of the above method of forming a solution the following may be used :—

Copper tartrate	120 grains
Sodium hydrate	160 ,,
Water	4 fluid ounces.

This solution acts precisely as the former one.

§ 277. Stölzel coppers various metals by using a paste

consisting of cream of tartar, copper sulphate, and water. The following proportions were tried :—

Copper sulphate	1 part.
Water	4 parts.
Cream of tartar	to form a thin paste.

The paste was then brushed on to the work with a hard brush. Sheet iron, cast iron, and tin were well coppered by this means. Zinc received a black deposit. Brass was unaffected. Upon tin the best result appears to be obtained by smearing the paste upon the surface, allowing it to remain a few minutes, then washing it off with water, and scratch-brushing. In all cases scratch-brushing renders the deposit paler.

§ 278. An excellent method of coppering zinc, which has the great advantage of cheapness, is adopted by the author, who uses the blue deposit which accumulates at the bottom of vessels containing aquafortis, in which brass and copper goods are dipped or pickled, and which is known as blue-stone. The proportions recommended are—

Blue-stone . . .	500 grains.
Water	20 fluid ounces.
Ammonia . . .	to neutralise the free acid.

The precipitate formed by the addition of ammonia is readily dissolved when the alkali is added in excess.

Zinc quickly receives a good bright deposit of copper. Iron, tin, and brass are quite unaffected when immersed alone in the solution; if placed in contact with zinc a coating of copper is obtained, but only on the parts which actually touch the zinc, so that the method is only adapted for zinc.

In preparing this solution for coppering zinc care must be taken to avoid having a large excess of ammonia, as when too much of this latter reagent is present the deposit is black instead of reguline. If too much ammonia should have been added the fault may easily be corrected by adding more of the copper salt and water in proportion.

Brass may be coppered by using the above solution without the addition of ammonia. It is necessary, however, to have the artiele in contact with a piece of iron, or better still, to well wrap iron wire round it. When the coppering is complete the brass should be thoroughly swilled in clean water and dried out in sawdust.

Small steel and iron articles may be coppered by simple immersion in a solution of

Blue-stone	1 part.
Water	20 to 30 parts.
Sulphuric acid	1 part.

Or they may be buried in sawdust which is kept well moistened with the coppering solution.

Large iron articles, after thoroughly cleaning, are best painted with a saturated solution of sodium hydrate, then with a saturated solution of the blue-stone. The same precaution must be taken as before described to ensure uniformity.

BRASSING ARTICLES BY SIMPLE IMMERSION

§ 279. According to Baceo, a solution of equal parts of copper sulphate and zinc sulphate, to which a solution of potassium cyanide has been added until the precipitate which first forms has been redissolved, and then a little

ammonia poured in, gives a deposit of brass on zinc articles by immersing them during the space of twenty-four hours.

Take the following proportions :—

Copper sulphate	4 ounces.
Zinc sulphate	4 ,,
Water	1 gallon.

Dissolve the two salts in a portion of the water, then add potassium cyanide as directed above, and one-tenth its volume of ammonia. Dilute to one gallon. If a lighter shade of brass is required, take

Zinc sulphate	8 ounces.
Copper sulphate	4 ,,
Water	1 gallon.

In our experiments, using the above solution, a very good coating of brass was obtained in about two hours; if left in longer the deposit became too red in colour, resembling copper. The solution was found to work much better cold than hot, as the coating which is first obtained is dissolved again in the hot solution, especially if there is much free potassium cyanide and ammonia present.

§ 280. A simple immersion brassing solution is recommended by Ludersdorff as follows—

Copper sulphate	250 grains.
Water	3 fluid ounces.

The copper sulphate is dissolved in the water, and a solution of washing soda added to precipitate the copper as carbonate. This is filtered off, well washed with water, and dissolved in a solution of cream of tartar. Three grains of ammonium chloride is then added to each fluid ounce of the solution, when the liquid is ready for use.

In working with such a solution we obtained a dark reddish-coloured deposit on zinc immediately it was immersed. The colour at the beginning was about the colour of an old bronze penny, but not uniformly distributed. On taking the article out of the solution it became nearly black in parts. On scratch-brushing the deposit was removed and the zinc surface exposed.

§ 281. A good deposit of the colour of brass may be rapidly obtained on zinc by immersing it in a solution of

Copper tartrate	50 grains.
Sodium hydrate	380 ,,
Water	1 fluid ounce.
Cream of tartar solution	5 ,, ounces.

The coating is improved by scratch-brushing. If clean iron articles are immersed in the above solution they are soon coated with a thin film of copper.

If less cream of tartar is added than that given above, so as to form a thin paste instead of a solution, and the paste is applied to the zinc articles by means of a vigorous rubbing, they become rapidly coated with copper. The same remarks apply to iron goods. If the coppered brass articles are heated in an oil-bath to about 150° C., the copper and zinc near the surface seem to unite to form a layer of brass.

COATING METALS WITH TIN

§ 282. Many metals are coated with tin, because that metal prevents the base which it covers from being oxidised. It is often applied direct in the metallic state, but it may also be deposited very readily from its solu-

tions by simple immersion, or by contact with another metal. The salt of tin most commonly used, in consequence of its solubility, is the chloride. Stannous chloride is the most useful salt, and should be made as required, by dissolving the metal in hydrochloric acid, as the salt becomes less soluble after standing for a long time.

Sodium and potassium stannate solutions may be also made by dissolving these salts in water, or by boiling tin oxide in a strong solution of sodium or potassium hydrate. The same liquid may be produced by passing a current of electricity through a solution of sodium or potassium hydrate, using a large tin anode. This solution decomposes by exposure to the atmosphere, and deposits tin oxide at the bottom of the vessel.

A very interesting example of the deposition of tin may be seen by immersing a rod of zinc in a dilute solution of stannous chloride, to which a few drops of nitric acid have been added, and allowing the whole to remain undisturbed for some time.

§ 283. C. Paul uses the following solution for tinning zinc, iron, brass, copper, etc. :—

Water	10 parts.
Sulphuric acid	1 part.
Copper sulphate	1 part.

A dilute solution of copper sulphate is added to the acidified water with stirring after the articles have been immersed. When they have become coated with a thin layer of copper, they are removed, washed, and then wetted with a solution of

Stannous chloride	1 part.
Water	2 parts.
Hydrochloric acid	2 ,,

They are next shaken with a mixture of finely-powdered chalk, copper sulphate, and ammonium sulphate, which is prepared by dissolving one part of copper sulphate in sixteen parts of water, and adding ammonia until a clear dark blue liquid results. The articles are now tinned by immersion in a solution of

Stannous chloride	1 part.
Cream of tartar	3 parts.
Water	to form a solution.

§ 284. The following method is simpler than the above:—

Stannous chloride	1 ounce.
Cream of tartar	2 ounces.
Water	5 fluid ounces.

Zinc and lead are tinned by simple immersion, but there is also deposited a pasty mass of tin, which rubs off, leaving a thin reguline and firmly adherent deposit of tin on the surface.

Iron, brass, bronze, and copper are tinned in this solution when in contact with zinc; the deposit extends uniformly over the surface, and withstands scratch-brushing.

It would appear, from the rapid precipitation of tin by zinc, that zinc should only have a very short immersion in this solution, and be worked at the ordinary temperature.

§ 285. Gore recommends the following solution for coating articles of iron or zinc with tin:—

Stannous chloride	1 part.
Ammonium alum	30 parts.
Water	1000 ,,

Heat the solution to boiling and immerse the previously

cleaned articles in it until they attain a fine white colour, and add fresh stannous chloride as the solution becomes weaker.

Zinc and lead are well tinned in the above solution. Brass, iron, bronze, and copper may be tinned if placed in contact with zinc, but the deposit only occurs on the side adjacent to the zinc, so that the articles must be completely surrounded by that metal if they are to be tinned all over. Zinc and lead should not be allowed to remain in the solution longer than is absolutely necessary to obtain a good reguline deposit, as beyond this point the tin is deposited in a pasty mass.

§ 286. According to Roseleur, articles of zinc may be tinned by simple immersion in a solution composed of

Fused stannous chloride	1 part.
Sodium pyrophosphate	5 parts.
Water	300 ,,

We found this solution to work very slowly indeed; after several hours' immersion a black deposit was formed, and on scratch-brushing a coating of tin was revealed. Iron and steel were well and rapidly coated in this solution by placing in contact with zinc.

§ 287. Roseleur also recommends the two following liquids for coating iron articles by zinc contact:—

I.	Cream of tartar	1 part.
	Stannous chloride	1 ,,
	Water	1 ,,
II.	Stannous chloride	6 parts.
	Sodium pyrophosphate . . .	60 ,,
	Water	3000 ,,

Each liquid must be used hot and kept in constant motion. The articles are immersed in contact with fragments of zinc, the entire surface of which should be equal to about one-thirtieth that of the articles to be tinned. The operation lasts from one to three hours. Roseleur gives the preference to No. II. solution. He also prefers to use coils of zinc instead of fragments of the metal, as being less liable to cause markings on the articles than the latter. For tinning small articles they are plaeed in layers on perforated zinc plates which must be quite clean before immersion.

§ 288. A solution for tinning may be made with

Stannous chloride (concentrated solution)	½ fluid ounce.
Water	5 ,, ounces.
Sodium hydrate	in slight excess.

Zinc is tinned in this solution by simple immersion, but not so well as in the previous methods. Brass and iron are tinned by zinc contact.

COATING METALS WITH ZINC

§ 289. Articles to receive a deposit of zinc must be thoroughly clean, especially iron castings, and frequently moved about in the bath while the deposition is proceeding. They should also be well scratch-brushed during the process with a steel brush. Polishing is effected by means of the usual calico bobs, using lime and oil.

I. For zincing iron by contact a concentrated solution of zinc chloride and ammonium chloride is suitable. The

liquid is boiled and the objects immersed in contact with large surfaces of zinc.

II. Boil commercial zinc powder with a concentrated solution of sodium hydrate, then immerse the articles to be zinced in the boiling solution, when they will soon become covered with a bright layer of zinc. Copper articles are best put in contact with a piece of zinc.

PART V

MECHANICAL METAL-COLOURING

§ 290. Colours may be imparted to various objects by which an imitation of bronze may be obtained, by adding to the surface a mere mechanical deposit which is not an integral part of its substance, and therefore not a true bronze, but simply a second substance imposed on the surface.

This may be well illustrated by the method of bronzing with Dutch-metal powder. (The scraps obtained from beating the metal to form the thin sheets known as *leaf* are rubbed with honey or gum to form the powder.) The body to be bronzed is first varnished with japanner's gold-size, and the metal powder applied to the surface by means of a pad of chamois leather.

§ 291. A coating of gold may be also imparted to articles in a similar way. Leaf-gold is ground with virgin honey on a stone until the leaves are broken up and minutely divided. The mixture is removed by means of a spatula and stirred up in a basin of water, whereby the honey is dissolved and the gold set free. The basin is then left undisturbed until the gold subsides, the water is poured off, and fresh quantities added until the honey

is entirely washed away, after which the gold is collected on a filtering paper, and dried for use.

The gold-size is applied to the perfectly clean and dry article by means of a brush, carefully going over the whole again to remove any excess of size that may have lodged in any of the crevices. Now allow it to remain in a clean and warm place for several hours until it is just sticky but not liquid, then apply the gold powder or bronze powder as the case may be.

§ 292. Instead of Dutch-metal leaf, tin sulphide may be used as a bronzing powder. One part of tin sulphide is rubbed with six parts of bone-ash, and the mixture applied to the objects by means of a moist linen pad.

Copper which has been precipitated by means of iron may be also employed, as well as various alloys of copper and zinc, and copper and tin, after being reduced to a very fine state of division.

White bronze powder may be obtained from an alloy of equal parts of bismuth, tin, and mercury, known as Mosaic silver, which, being of a very brittle nature, can be readily crushed to powder. Instead of this alloy metallic tin may be used. It is reduced to powder by pouring it into a box, the inside of which has been well rubbed with whiting, and when the metal is just on the point of solidifying, vigorously shaking, when the metal breaks up into an exceedingly fine powder. The coarser fragments are removed by means of a fine sieve. The finely-sifted portion is made into a thin paste with liquid glue and applied to the object by means of a brush. This produces a dead colour which may be made bright by means of a burnisher.

A gray tint may be imparted to objects by first giving

them a coating of blacklead and then applying the preparation of white bronze.

But it is quite unnecessary to deal further in this work with the manufacture of bronze powders, as they are manufactured on the large scale, and can be so cheaply purchased in all shades of colour that no bronzer would dream of making them for himself.

§ 293. Böttger recommends the following method for bronzing wood, porcelain, glass, etc. :—

A concentrated solution of potassium silicate is first prepared, and the articles are coated with it in as thin and as uniform layers as possible by means of a brush, or if the articles are small, they may be immersed in the solution. While the articles are still moist, bronze powder is applied, and then they are left to dry in the air at the ordinary temperature, when any superfluous powder is removed by a soft brush. The layer of bronze powder adheres very firmly to the object, and may be polished or burnished.

Böttger states that this method is very well adapted for articles of iron or porcelain which have to be subjected to heat, as the bronze is not altered by a moderate increase of temperature. The frames of mirrors, or tables, gilt either with real or imitation gold, which have been damaged by use and had their gilding removed, may be repaired by means of this process, using gold or bronze powder as desired. Glass, wood, and many other bodies may be easily decorated by this process.

§ 294. **Materials for Bronzing as used by Japanners.**—*Metallic Bronze Powders.*—These may be purchased in almost any required colour at prices varying from about three shillings to thirty-two shillings per pound. The

cheapest quality is used for bronzing common cast-iron work, and the better qualities for a superior class of goods. For general purposes that sold at seven shillings per pound and retailed at sixpence per ounce is usually preferred.

The colours commonly kept in stock by retailers are white (imitation silver), various shades of imitation gold, such as pale, deep, and green gold respectively; various shades of crimson or copper bronzes, as well as all shades between crimson and green gold, including orange, citron, etc. Besides these well-known bronze powders others have been more recently introduced possessing very brilliant tints, probably produced by dyeing the metallic powders with aniline dyes.

Varnishes.—The varnish used for fixing the bronze powders is called gold-size, of which two kinds are in general use, viz. quick-size and slow-size. The former dries or becomes *tacky* (in which condition it is suitable to receive the bronze powders) in about fifteen minutes after the work has been varnished with it, whilst the latter will require several hours to arrive at the same condition.

The varnish used to protect the work from oxidation after bronzing is that known as *copal* varnish. Several qualities are used by japanners. A nearly colourless varnish must be used for light or richly tinted bronze work, but a darker and cheaper variety may be employed for the darker-coloured work. The price varies from six to sixteen shillings per gallon.

Turpentine.—This is used for thinning the different varnishes used by japanners.

§ 295. **Bronzing Operation.**—All work, except that of

the commonest kind, is japanned and dried in a stove before being bronzed. The method adopted depends on the kind of work to be done.

Iron furniture castings, of the common kind, are varnished all over with gold-size and set aside until they are nearly dry or "tacky," when the bronze powder is rubbed on the relief parts by means of a leather pad. The articles are then put into a stove or oven, where they are allowed to remain until the gold-size dries perfectly hard. They are then coated with copal varnish and returned to the stove to again dry. In some cases the metallic bronze powder is mixed with gold-size to the consistency of paint, and this is brushed on to the relief parts of the work, which is dried in the stove, and not subsequently varnished; this method is not nearly so effective as the one previously described.

Castings for superior kinds of work are treated as follows:—Instead of painting the gold-size all over the casting, the operator pours a little out upon his stone, and grinds just sufficient chrome-yellow into it to impart a yellow tint. He then applies the tinted varnish to the work by means of a camel-hair pencil, carefully following the outlines of the part to be bronzed. The object of tinting the varnish is to enable the workman to see the parts that have been outlined. This operation is termed "picking out." As in the first method, the bronze powder is rubbed in after the size has acquired the proper degree of stickiness, and the work is then stoved and varnished.

Bronze powders are much used in ornamenting japanned and polished work, such as cash-boxes, tea-trays, etc. In this case the artist, or japanner as he is called, draws the

design upon the surface of the work with a camel-hair pencil by means of the tinted varnish, and when this is sufficiently dried the bronze powder is rubbed in, using one or several colours, when the operation is finished as described above.

§ 296. Bronze filleting is done as follows :—The work, say a cash-box, has a band or fillet, about one inch wide, drawn around the lid at a distance of half an inch from the edge, and when this is sufficiently dry, pale imitation gold-bronze powder is rubbed in and dried in a stove as before. The black japanned box lid now presents the appearance of having a brass band inlaid upon it. The box is now returned to the japanner, who binds the edges of the bronze band with a fine sharply drawn line also in tinted varnish, he also draws other fine lines around the body of the box, and when all these lines have acquired the right degree of stickiness by drying, he rubs in bronze powder, but of a different colour to that used for the fillet. Copper-bronze powder is generally used for this purpose. The work is then returned to the stove and varnished as usual. The fillet now appears like a brass band bound with narrow copper edges, whilst the copper lines upon the body of the box give a finished appearance to the work.

§ 297. For most purposes the slow japan gold-size is preferred, because a large quantity of work can be sized one evening and be ready for the application of the bronze powder on the following morning. If quick-size were used instead of slow-size the bronze powder would have to be rubbed in soon after the sizing, as it would be too dry after standing all night. The bronze powder fixed with slow-size is also less liable to become "shady" than that fixed with quick-size.

Gold-leaf and Dutch-metal leaf is also used in conjunction with bronze powders for decorative purposes. The method of fixing the metal upon the work is precisely similar to that described for bronze powders, except that the gold or metal leaf is laid carefully on the sticky pencilled design, gently pressed down with a pad, and, as the leaf adheres only where the design has been drawn, the excess is wiped off with a silk duster.

The gold scrap is carefully collected and sold to the refiners. The metal scrap is sold to the bronze-powder makers.

Gold-leaf is sold in books, about 1s. 3d. each, each book containing twenty-five leaves. Dutch-metal leaf costs from 1d. to 3d. per book of twenty leaves.

§ 298. When the gold-leaf upon the work is required to have a beautifully bright surface, or to be burnished as it is called, the process is conducted as follows :—

The japanned surface of the work to be gilded bright is previously highly polished. The japanner first wets the surface of the work with a solution of isinglass, and then cuts the gold-leaf into strips of suitable width, which he places carefully upon the prepared surface. The excess of islinglass solution is then drained away, and the gold adheres firmly to the work.

The design is next drawn upon the surface of the gold with a camel-hair pencil, using black asphaltum varnish for this purpose. When the design is finished and dry, the gold not covered by the varnish is removed by gently rubbing with cotton wool moistened with water. The varnish being insoluble in water protects the gold, which is to constitute the decoration, from being injured by the process.

The next step is to remove this varnish so that the gold beneath shall be exposed to view. To do this the varnish is washed off with turpentine, in which liquid it is easily dissolved, whilst the isinglass which binds the gold to the work is unaffected because it is insoluble in turpentine.

The design now appears in gold and only requires to be gently rubbed with chamois leather and whiting to give it a brilliant lustre. In this condition it could easily be washed off with water, because isinglass is soluble in water. To prevent this, the entire gilt surface is coated with one or two layers of colourless copal varnish, which is dried hard in a japanner's stove, after which it affords a permanent protection to the metal.

Gold-leaf is beaten exceedingly thin, hence when a burnished appearance is desired it must be laid upon a bright surface. If the gilding is done upon a dead surface the gold will be correspondingly dead.

As in the case of bronze powders gold-leaf can be obtained in several shades of colour, such as pale gold, deep gold, and green gold; the two first being formed by alloying gold with different proportions of copper, and the other by alloying gold with silver.

§ 299. **Bronzing of Plaster of Paris Articles.**—The bronzing of articles made of plaster, terra-cotta, wood, and other non-metallic substances may be effected in various ways; and although it is with the colouring of metals that this work is chiefly concerned, it has been thought advisable to give some information with regard to the colouring of other bodies. In many cases metals are electro-deposited on non-metallic surfaces, and then the subsequent bronzing is a colouring of the deposited metal.

§ 300. According to Thénard and D'Arcet, plaster figures may be bronzed with a green patina in the following way :—

1st. Boil some linseed oil with caustic soda, so as to form a neutral soap; then add a concentrated solution of common salt, and boil until grains of the soap swim on the surface. Filter and well press the precipitate until all the lighter particles are removed; then dissolve the soap in distilled water and filter off any insoluble residue.

2d. Prepare a clear solution of 4 parts copper sulphate and 1 part iron sulphate, boil, and add a little at a time a portion to the above soap solution, and well boil. Wash the precipitate and add it to the remaining solution of sulphates. Well wash the precipitate by decantation with hot water, then with cold water, and finally filter it off.

Take 3 parts of boiled oil, $1\frac{1}{2}$ parts of the above prepared soap of copper and iron, and 1 part of pure white wax, and melt the whole together. Heat the plaster figure to about 80° C., and apply the molten mixture. If the article is small, it may be immersed in the composition, then removed and dried at 80° to 90° C. The operation is repeated until the plaster will absorb no more of the liquid; it is then left to stand exposed to the air until all odour disappears, and finally rubbed with a pad of fine linen.

§ 301. Another method of coating plaster objects with a green bronze is to paint them first with a solution of copper acetate containing some plumbago in suspension (4 of copper acetate to 1 of plumbago), and when this is dry to give them a coating of gum, and lastly a coating of gold-size. Bronze powder is then rubbed on the prominent parts and the whole brushed with a waxed brush when dry. Six parts of copper acetate are now dissolved in vinegar,

1 part of yellow chrome added, and 1 part of plumbago. This mixture is painted on with a brush so as to leave the deep parts green. After standing for five or six hours, the article is coated with a transparent varnish, and the prominent parts relieved if necessary with bronze powder.

It will readily be understood from the preceding that a great variety of tones may be imparted by means of different bronze powders and mixtures, which are coloured when dry.

§ 302. An iron colour may be imparted to plaster articles as follows—

Digest in the essence of terebinth 2 parts of red iron oxide and 1 part of soot, heat on a sand bath and add a little yellow wax. This mixture is painted on the plaster article with a brush, and the object dried in a stove. When the object has absorbed the fat part of the coating, a little brown umber is sprinkled on to imitate rust in the deeper parts, and white bronze on the prominent parts, the powders being fixed with gold-size in the usual way. Particular parts may be relieved by rubbing with the finger. Other coloured powders may be added if desired.

§ 303. A red bronze may be produced on plaster figures by the method described in § 300, by increasing the proportion of soap of iron or omitting the copper. Or in a solution of strong glue to digest some Prussian blue, soot, and yellow ochre. The article is coated several times with this mixture, with alternate drying. Lastly, any special parts may be touched up with a fine brush which has been dipped in tin sulphide and varnish.

§ 304. Many colours on so-called bronze objects are simply produced by different pigments, such as those on the draperies of figures, wings of birds, skins of animals, etc.

A common method is to paint with two or three coats, allow to dry, then give a coating of varnish or simply of the white of an egg.

A golden-yellow is produced from a decoction of the young root of the hawthorn mixed with a little saffron.

Green is obtained by boiling some *night-shade* in 1 part vinegar and 1 part water.

Red is produced by boiling some Brazil wood with alum, and the same boiled with caustic soda is used to produce a brown. The colours are applied by means of a varnish.

Plaster figures are made to imitate silver by means of an amalgam of mercury, tin, and bismuth, then coated with a transparent varnish.

§ 305. The best means of imitating bronze on plaster articles is to deposit a coating of copper or brass on their surfaces by means of the electric current. The whole surface must first be saturated with boiled linseed oil and allowed about two days to dry. The surface is then brushed over with a concentrated alcoholic solution of silver nitrate, allowed to dry, and submitted to a current of sulphuretted hydrogen, which converts the surface into a coating of silver sulphide, and this being a good conductor of electricity, enables the metal to be deposited when the article is placed in the depositing bath.

REMEDIES FOR ACCIDENTS, ETC., IN PROCESSES OF BRONZING

§ 306. As some of the substances referred to in the text are of a highly poisonous nature, and others have an injurious influence on the flesh, when the skin happens to be broken, it is desirable to know what to do in case of an accident.

Workmen exclusively engaged in pickling objects are advised to neutralise the action of acid vapours upon the enamel of the teeth and the mucous membranes of the mouth and throat by frequently rinsing the mouth with a dilute solution of sodium carbonate.

In cleansing articles from grease by means of caustic potash or soda, the skin may be irritated and made very sore, especially if any part is cut or broken. The operator should frequently swill his hands in clean water, and, previous to each repetition of the immersion, dip them in a very dilute solution of sulphuric acid, dry them, and well rub with equal parts of glycerine and water. It is advisable, in the case of a cut finger, to cover the wound with plaster, and well wrap it round with some linen rag.

Great care should be exercised with the drinking-vessels used by the workmen in a plating or bronzing shop, as many cases of poisoning have occurred from want of

thought in this direction. There is a great temptation in cases of emergency to use the same jug or cup for ladling out a solution as is used for ordinary drinking purposes, and if such a vessel is not properly swilled out serious consequences may follow.

Many individuals are very sensitive to nickel solutions, eruptions, which are very painful and heal slowly, breaking out upon the arms and hands. In case such a person has to touch nickel salts, or to put his hand into a nickel solution to remove an object which has fallen to the bottom of the bath, he should immediately well wash his flesh with clean running water.

In cases of internal poisoning the following plans should be pursued, as everything depends on promptitude in applying the remedy :—

Poisoning by Nitric, Hydrochloric, or Sulphuric Acids.—Administer abundance of tepid water to act as an emetic, or swallow milk, the whites of eggs, some calcined magnesia, or a mixture of chalk and water. If those acids, in a concentrated state, have been spilled on the skin, apply a mixture of whiting and olive oil. If the quantity is very small, simple swilling with plenty of cold water will suffice. A useful mixture, in case of burning with strong sulphuric acid, is formed with one ounce of quicklime slaked with a quarter of an ounce of water, then adding it to a quart of water. After standing some time pour off the clear liquid and mix it with olive oil to form a thin paste.

Poisoning by Potassium Cyanide, Hydrocyanic Acid, etc.—If cyanides, such as a drop of an ordinary plating solution, has been accidentally swallowed, water, as cold as possible, should be run on the head and spine of the

sufferer, and a dilute solution of iron acetate, citrate, or tartrate administered. If hydrocyanic acid vapours have been inhaled, cold water should be applied as above, and the patient be caused to inhale atmospheric air containing a little chlorine gas. It is a dangerous practice to dip the arms into a plating solution to recover any work that has fallen off the wires, because the skin often absorbs cyanide liquids, causing painful sores. In such a case well wash with water, and apply the olive oil and lime water mixture.

Poisoning by Alkalies.—These bodies are the opposite of acids in character, so that acids may be used as antidotes. It is preferable to employ weak acids, such as vinegar or lemonade; but if these are not at hand, then use exceedingly dilute sulphuric acid, or even nitric acid diluted, so that it just possesses a decidedly sour taste. After about ten minutes, take a few teaspoonfuls of olive oil.

Poisoning by Mercury Salts.—The white of an egg is the best antidote in this case. Sulphur and sulphuretted hydrogen are also serviceable for the purpose.

Poisoning by Copper Salts.—The stomach should be quickly emptied by means of an emetic, or in want of this, the patient should thrust his finger to the back of his throat so as to tickle the uvula, and thus induce vomiting. After vomiting drink milk, white of an egg, or gum water.

Poisoning by Lead Salts.—Proceed as in the case of copper salts. Lemonade, soda water, and sodium carbonate are also serviceable.

Poisoning by Acid Vapours.—Admit immediately an abundance of fresh air, and inhale the vapours of ammonia, or a few drops of ammonia may be put into a glass of water and the solution drunk. Take plenty of hot drinks and

excite warmth by friction. Employ hot foot-baths to remove the blood from the lungs. Keep the throat moist by sipping milk.

§ 307. **Removal of Stains, etc.**—To remove stains of copper sulphate, or salts of mercury, gold, silver, etc., from the hands, wash them with a very dilute solution of ammonia, and then with plenty of water; if the stains are old ones, they should be rubbed with the strongest acetic acid, and then treated as above.

Grease, oil, tar, etc., may be removed from the hands or clothes by rubbing with a rag saturated with benzine, turpentine, or carbon bisulphide.

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